

ORIGINAL CONTRIBUTION

RECOVERING OF COMPONENTS FROM
PLASTIC BONDED PROPELLANTSManfred A. Bohn,^{1*} Rainer Schweppe¹ and Werner Weisweiler²¹Fraunhofer-Institut für Chemische Technologie (ICT), Postfach 1240, D-76318 Pfinztal, Germany²Institut für Chemische Technik, Universität Karlsruhe, Kaiserstraße 12, D-76128 Karlsruhe, Germany

ABSTRACT. Economic reasons and the protection of the environment demand methods of disposal allowing to recover and re-use materials, which have been in service as well as to avoid producing unwanted or harmful substances when doing so. This also applies for propellants and explosives. Recently developed propellants contain expensive crystalline energetic materials such as the nitramines, hexogen (RDX) and octogen (HMX), bonded in a chemical three-dimensional crosslinked polyurethane matrix. These substances are called “plastic bonded propellants”. In order to recover the components, the polyurethane matrix is broken solvolytically with pure water and alkaline water (0.05 n–0.5 n NaOH) at temperatures between 130 and 170°C in a pressure cell. From a model rocket propellant, consisting of a polyetherpolyol mixture (Lupranol 1000/2021) cured with Desmodur T80 and filled with 60 mass% ammonium perchlorate (AP), 84–90% of the polyetherpolyol component was recovered, and 98% of the AP content subsequently determined in the aqueous solvolysate. The polyetherpolyols were nearly not changed at the high solvolytic stress of 170°C and 2 h, as shown by the molar mass distributions, determined by using gel permeation chromatography. The solid gun propellant KHP consisting of 86 mass% hexogen (RDX) and 14 mass% GAP-N100 binder was solvolyzed at 130, 150 and 170°C with pure water and with 0.05 n NaOH for corresponding time periods of 10, 30 and 60 min. Hexogen is recoverable with high yields and with high purity. GAP (glycidyl azide polymer) is a polyetherdiol as Lupranol 1000, formally on the basis of propane-1,2-diol with azide (N₃) groups attached to its lateral methyl groups. It does not behave in the same way as the Lupranol polyetherpolyols. Under exposure to solvolytic conditions, its molar mass distribution is broadened and its azide content is reduced, which was determined via infrared absorption of the asymmetric N₃ stretching vibration, and via its energy content using DSC, in both cases in relation to the azide content of the unexposed GAP. The GAP-N100 binder is not split up, GAP is not recoverable. In the splitting-off of nitrogen from the N₃ group, a nitrene functionality arises which forms solvolytically not scissionable C–N bonds by intermolecular insertion reactions. The gaseous main reaction products in the solvolysis of KHP are N₂ and N₂O, besides a little CO₂, O₂ and CO. NH₃ and CH₂O were not quantified. The following ionic decomposition products were found: NO₂⁻, NO₃⁻, HCOO⁻ and NH₄⁺. The product spectrum can be interpreted from the mechanisms and reaction products given in the literature for the decomposition of hexogen, as well as through reactions of the decomposition products with the solvolytic agent and reactions among the decomposition products themselves. © 1997 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

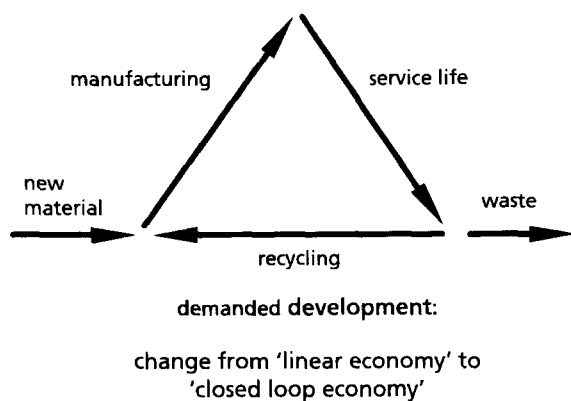
For the disposal of propellants and explosives, the following possibilities come under consideration: burning, hydrolytic decomposition, conversion in supercritical water (also with additional use of oxygen), re-use and selective recovery of components. In the burning of propellants and explosives, toxic gases are always produced, such as HCN (this is oxidized with excess oxygen), NO_x, HCl and soot in considerable quantities,¹ so that a technical and

monetary fume cleaning process is necessary. As a result of the new laws on waste reduction and material reprocessing, disposal processes facilitating recovery and re-use are very much in demand,² Fig. 1 shows in a schematic illustration the intention of the new regulations and laws. The crystalline energetics hexogen and octogen are expensive components, their actual price per kg is about 35 DM and 100 DM (18 and 50 US\$). The prepolymers used for three-dimensionally crosslinked polyurethane elastomer binders are also expensive, HTPB (hydroxy terminated polybutadiene) costs approx. 20–25 DM kg⁻¹ (10–13 US\$), and the price of GAP (glycidyl azide polymer) is still over 700 DM kg⁻¹ (350 US\$). One can define a degree of suitability R_A for the recovery or recycling of a material in the following way:

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The material cycle for a product



as a part of the 'sustain(ing) development'

FIGURE 1. Schematic illustration of the intention of the new regulations and acts dealing with recycling and waste disposal.

$$R_A = \frac{\text{cost of new material} + \text{cost of non-recycling disposal method}}{\text{cost of dismantling} + \text{cost of processing} + \text{cost of logistics}}$$

If R_A is greater than one the recovery is economical. This quantity is already used in the automotive industry to assess the car construction materials in order to manufacture an environmentally acceptable (compatible) car. At BMW company, Munich, the bumper material has a R_A value of 2.1 with a price for the new material of 5.50 DM kg⁻¹ (2.8 US\$), so the recycling is far in the economical range.³

On account of the three-dimensional chemical crosslinking of the polyurethane matrix, a simple disintegration of the propellants by solvents is not possible. For a recovery of energetic materials, the choice has to be found between extraction with solvents and a solvolytic break-down of the plastic binder with a release of the energetic material. In a solvolytic break-down process, the polyol components of the polyurethane binder become accessible. The results of such a process are presented below. In part extraction is also present in the solvolysis process.

The energetic substances used in propellants such as GAP and hexogen (RDX) show autoignition temperatures between 200 and 220°C. The solvolysis temperatures must therefore be lower, a range between 130 and 170°C was chosen here. The ideal solvolysis agent should be able to split the urethane groups rapidly, should leave the chain lengths of the polyols unchanged, should not attack the energetic components, and should be easily removeable from the recovered substances. In the context of technical realization, the process ought to be safe and inexpensive. Pure and alkaline water meet this profile of requirements best of all. To make the solvolysis possible within the selected temperature range, it is necessary to enclose the solvolytic mixture in a pressure cell.

2. OBJECTIVE

Hexogen (RDX) bonded with GAP, which is cured with isocyanate Desmodur N100, is to be recovered from a propellant via aqueous solvolysis. The yield is determined as a function of the solvolytic agent (pure water and 0.05n NaOH), the temperature of solvolysis (between 130 and 170°C), and time period of solvolysis. The influence of the solvolytic conditions on the polyol component GAP is investigated, and compared with the results from a non-energetic polyetherpolyol component. The gaseous and ionic decomposition products are determined.

3. SUBSTANCES

For the solvolytic processes several binder components and propellants were used. A gun propellant KHP with medium grain size (2 mm in diameter, 4 mm long) was used, which contains about 86 mass% fine-grained RDX bonded in 14 mass% GAP-N100 binder. The GAP and the KHP were manufactured at the ICT.⁴ The RDX was purchased from Dyno Industrier AS, Saetre, Norway, and the isocyanate Desmodur N100 from Bayer AG, Leverkusen, Germany. GAP is a polyetherdiol, formally a condensed propane-1,2-diol with azide groups attached to the lateral methyl groups. For comparison, a plastic binder made from the commercially available polyetherpolyols Lupranol 1000 and Lupranol 2021 (BASF AG, Ludwigshafen, Germany) was prepared, the curing agent was the isocyanate Desmodur T80 (a mixture of 80 mass% 2,4- and 20 mass% 2,6-toluenediisocyanate, Bayer AG, Germany). The binder consisted of 78.8 mass% diol Lupranol 1000, 11.7 mass% triol Lupranol 2021 and 8.3 mass% Desmodur T80, the remainder are some auxiliary substances. With this binder type, the model rocket propellants FTS-1 with 60 mass% ammonium perchlorate (AP) and FTS-2 without AP were made.⁴

4. APPARATUS

The solvolyses were carried out in a cylindrical pressure cell, (Fig. 2) which had been made at the ICT from a heat-resistant, anticorrosive stainless steel of the type Thermanit 4575 (1880 SST, material no. 1.4575).⁵ The cell body has a height of 140 mm and an outer diameter of 68 mm. Its inner volume is 44 ml, the inner diameter 23 mm. The reaction chamber was sealed with a Viton sealing ring fixed in a groove of the piston P. To measure the temperature, a sheathed thermocouple of type Fe/CuNi, soldered into a pressure connecting screw, is introduced into the reaction chamber by screwing it into the piston P. This makes it possible to use the temperature of the

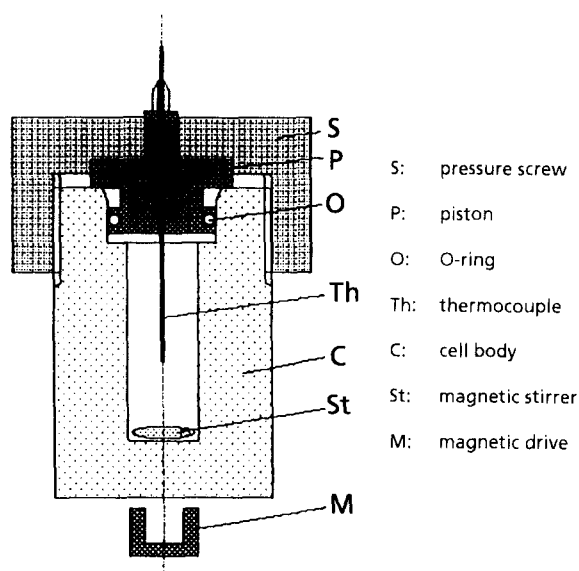


FIGURE 2. Scheme of the pressure cell.

solvolytic mixture for the control of the external electric heating system (resistance heating band wound around an aluminium case). The solvolytic mixture is kept in turbulence using a teflon-coated stirring magnet. The pressure is recorded using a pressure transducer and shown in the unit bar with a calibrated instrument (Burster GmbH, Gernsbach, Germany). The quantity of gas formed during the solvolysis is determined using a gas burette or a syringe-type gas sampling system.

5. CARRYING OUT OF SOLVOLYSES, TREATMENT OF SOLVOLYSATES AND ANALYSIS OF SOLVOLYSIS PRODUCTS

For the solvolytic processes, the reaction volume of the pressure cell was filled up to approx. 60% with the solvolytic mixture, which consisted of about 1 g shredded sample substance and 20 to 25 g solvolytic agent. The free reaction space was evacuated and filled up with helium to 1 bar. After the solvolysis, the pressure cell was cooled down to room temperature as fast as possible, the amount of gas produced was determined and samples taken for gas analysis. As solvolysate, an aqueous phase with ionic products is obtained and, in the case of KHP, a solid residue consisting of hexogen and binder. The aqueous phase was separated from the solid residue, and the hexogen washed out with acetone. The acetone was removed by drying and the dry residue weighed. From the solvolysis of the Lupranol binder an oily phase was also produced in addition to the aqueous phase, mainly consisting of released polyol, which was extracted with dichloromethane.

Apart from the gravimetric determination, the hexogen was also quantified using high-performance

liquid chromatography (HPLC). The HPLC analysis was done with a Waters system equipped with the Millennium 2010 data recording and evaluation system and the Waters photodiode array detector 996. The separating column was a reversed-phase column Type C-18, the mobile phase a water-methanol mixture.

The molar (molecular) mass distribution functions (MMD) of the Lupranols and of the GAP were determined using gel permeation chromatography (GPC). The apparatus consists here of the 1084B Hewlett Packard liquid chromatograph, the ERC 7510 ERMA refraction index detector and four Polymer Laboratories GPC columns connected in series with pore widths of 10^3 nm, 10^2 nm, 10 nm and 5 nm and a particle size of $10\ \mu\text{m}$. The eluent was tetrahydrofurane. The calibration was carried out with narrow distributed polystyrene standards.

The ions nitrite, nitrate, formiate and ammonium were analyzed using a GAT ion chromatograph with an Alltech Wescan 315 conductance detector. The columns were: a Wescan Anion/R-Column for NO_2^- and NO_3^- , a Wescan Anion Exclusion Column for the formiate, and a Wescan Cation/S-Column for NH_4^+ .

For the gas chromatographic analysis an apparatus from FISONs, Type GC 6000 VEGA, Series 2 was used. The gases nitrogen, oxygen, methane and carbon monoxide were separated in a molecular sieve 5\AA (0.5 nm) column, carbon dioxide and dinitrogen monoxide with a Poropak Q column. The gas quantities were determined with a calibrated heat conductivity detector. The carrier gas was helium. The gases NO/NO_2 were quantified with an NO_x Analysator type 951A by Beckmann Instruments.

6. RESULTS AND DISCUSSION

6.1 Solvolysis of Inert Polyetherpolyol-Binder and of Solid Model Propellants made with this Binder

Two model solid rocket propellant samples and the polyetherpolyols used for them as binder, Lupranol 1000 and Lupranol 2021, were solvolysed for 2 h at 170°C with pure water, 0.1 n NaOH and 0.5 n NaOH. The initial weights were between 0.4 g and 1 g. Drastic conditions were intentionally chosen to provide a better recognition of a decomposing effect. Both, diol Lupranol 1000 and triol Lupranol 2021 remained practically unchanged, as the molar mass distributions (MMD) of the exposed and unexposed samples show (Figs 3 and 4). The values of the characteristic mean molar masses M_n (number average), M_w (mass average), M_z (Z average) and M_{max} (molar mass at maximum of MMD) were only shifted very slightly to lower values (Table 1).

The binder with 60 mass% ammonium perchlorate (FTS-1) and the pure binder (FTS-2) are completely

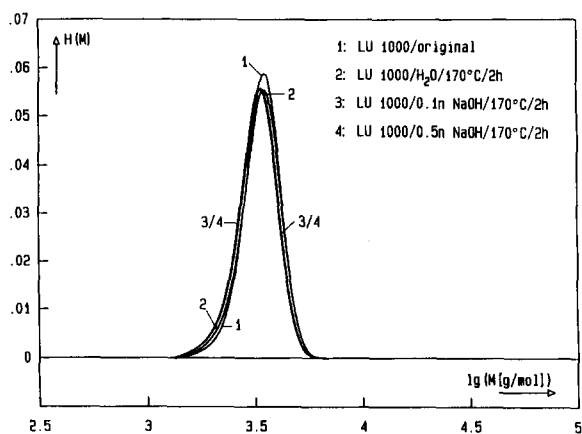


FIGURE 3. Molar mass distributions of the unexposed and solvolyzed polyetherdiol Lupranol 1000.

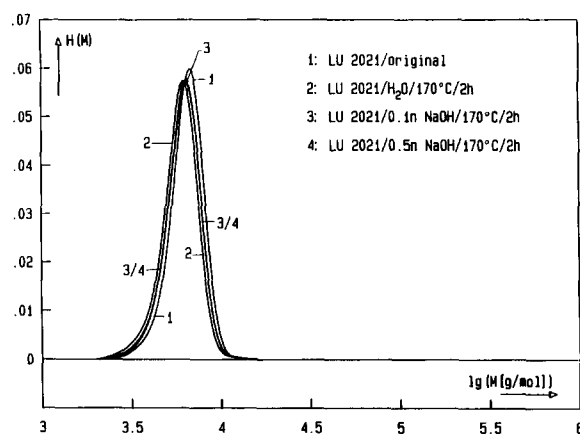


FIGURE 4. Molar mass distributions of the unexposed and solvolyzed polyethertriol Lupranol 2021.

decomposable with 0.5 n NaOH at 170°C. The polyol components are obtainable at high yields. On average 84% Lupranol is found from FTS-1, and over 90% from FTS-2. The quantity of ammonium perchlorate released was determined via the concentration of the perchlorate anion (by ion chromatography) and was 98%. In the case of FTS-1, a slight amount of gas was formed, approx. 8.1 ml gram⁻¹ FTS-1. No gas formation was observed in the other solvolytic processes. The MMD data of the Lupranols from FTS-1 and FTS-2 are shown in Table 1. Here too, the changes in MMD versus the unexposed polyols are very small.

6.2 Solvolysis of Energetic Polyetherpolyol-Binder GAP and the Determination of Azide Group Content of GAP
All solvolyses with uncured GAP were carried out at 170°C and 1 or 2 h solvolysis time. The solvolytic agents were pure water, 0.05n NaOH, heptane and toluene. All treated GAP samples were, as with the untreated GAP, soluble in dichloromethane. Compared with the results from the Lupranols the molar mass distributions of the treated GAP samples differed in a much more marked way to the distribution of the untreated GAP sample. The distributions became lower and broader and particularly the portion on the higher molecular side of the MMD increased (Fig. 5).

TABLE 1

Solvolyses of the Polyetherdiol Lupranol 1000, Polyethertriol Lupranol 2021 and Model Rocket Propellants (RP's) made with these Two Polyols at 170°C and 2 h

Sample	Solvolysis medium	Recovered Lupranol portion (%)	Molar masses in g·mol ⁻¹ from GPC			
			Mn	Mw	Mz	Mmax
Lupranol 1000	—	—	3280	3430	3560	3490
	Water	98	—	—	—	—
	0.1 n NaOH	79.5	3120	3280	3420	3380
	0.5 n NaOH	88	3100	3250	3390	3340
Lupranol 2021	—	—	6220	6540	6840	6790
	Water	97	5650	5990	6300	6250
	0.1 n NaOH	78	5880	6230	6550	6500
	0.5 n NaOH	85	5940	6250	6550	6470
Lu-RP-mixture	—	—	3190	3370	3530	3470
	—	—	6790	6940	7110	6490
RP-1 (with AP)	0.5 n NaOH	84	3330	3530	3720	3660
	—	—	6910	7030	7150	7010
RP-2 (without AP)	0.5 n NaOH	91	3330	3490	3650	3610
	—	—	7080	7320	7610	6920

The mixture Lu1000/Lu2021 was divided at the corresponding minima of the molar mass distributions.

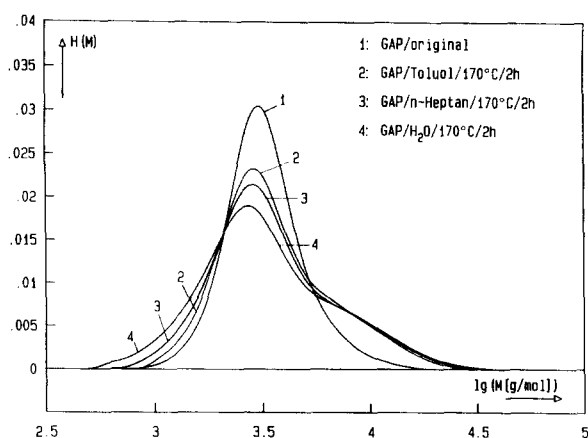


FIGURE 5. Molar mass distributions of the unexposed and solvolyzed azido-polyetherdiol GAP.

In order to characterize the solvolytically exposed samples, the azide group (N_3) content was determined with the infrared (IR) absorption of the asymmetric N_3 stretching vibration at 2100 cm^{-1} and via the energy content determined using DSC. The determination of the azide groups with IR was carried out according to a method already described.⁶ The specific absorption of the asymmetric N_3 stretching vibration was obtained with calibration solutions of untreated GAP in dichloromethane. To increase the accuracy, integrated band intensities were applied.⁷ As the high frequency half band is markedly disturbed but the low-frequency half band has disturbances only in the wing, integration was from the band maximum at 2104 cm^{-1} down to 2064 cm^{-1} .

The following applies according to Lambert-Beer:

$$A(\sigma) = \lg \frac{I_R(\sigma)}{I_S(\sigma)} = \varepsilon(\sigma) \cdot c \cdot l \quad (1)$$

σ	wave number (cm^{-1})
$A(\sigma)$	absorbance (extinction) (—)
$I_R(\sigma)$	intensity spectrum of reference sample
$I_S(\sigma)$	intensity spectrum of sample
$\varepsilon(\sigma)$	mass absorptivity (mass related extinction coefficient) (area/mass)
c	concentration (mass/volume)
l	geometric layer length (length)
\lg	decadic logarithm

In this case instead of the the molar absorptivity (mol related extinction coefficient) the mass absorptivity was used. The reference sample was dichloromethane. The spectra were recorded at a resolution of 4 cm^{-1} in a liquid cell with NaCl windows using a Fourier-Transform IR spectrometer from Nicolet, type 60SX. The layer length was $5.02 \times 10^{-3}\text{ cm}$. With the integrated intensity, equation (2), the decrease in N_3 -group content was determined relative to the content of untreated GAP according to equation (3).

$$B(\sigma) = \int_{\sigma_1}^{\sigma_2} \varepsilon(\sigma) d\sigma = \int_{\sigma_1}^{\sigma_2} \frac{A(\sigma)}{l \cdot c} d\sigma \quad (2)$$

$$\text{relative } N_3\text{-group content} = \frac{B(\sigma) \text{ of treated GAP}}{B(\sigma) \text{ of untreated GAP}} \quad (3)$$

The absolute N_3 -group content can also be determined by infrared absorption.⁶ The energy content of GAP is proportional to the N_3 content. The DSC thermograms, obtained with a heating rate of 2°C min^{-1} , were evaluated between 170 and 260°C . Untreated GAP releases an energy of 2447 Jg^{-1} . The ratio of the decomposition energy of the treated GAP samples to that of untreated GAP is a measure for the relative N_3 -group content. The results are listed together with the mean molar masses in Table 2. Both methods of determination agree well within their reproducibility, DSC $\pm 3\%$ and IR absorption $\pm 2\%$.

6.3 Solvolysis of GAP Cured with N100

The cured binder made from the polyetherdiol GAP and Desmodur N100 ought to behave solvolytically in the same way as the binder system Lupranol-Desmodur T80, that means it should be completely broken down in the same way. Solvolysis was carried out for one hour with 0.05 n NaOH at 170°C . However, the GAP binder does not behave in the same way as the Lupranol binder. An amount of only 1% of the initial weight, soluble in dichloromethane, was produced and the remaining solid residue could not be dissolved in common solvents including N,N -dimethylformamide. The cause for this is probably to find in a crosslinking by the stabilizing reaction of the highly reactive nitrene, which is formed by the splitting-off of nitrogen from the N_3 -group. The nitrene immediately performs intra- and intermolecular insertion reactions, thus producing the solvolytically non-scissionable C-N bonds. In the solvolytic process of GAP and the GAP-N100 binder, the production of gases could also be observed. The gases N_2 , N_2O were mainly found and small quantities of CO , CO_2 , O_2 as well as NO_x in ppm quantities. As regards ionic products, ammonium was detected. Table 3 shows the gas quantities given for 20°C , 1 atm and related to 1 g sample.

6.4 Solvolysis of Gun Propellant KHP

The KHP was subjected to solvolysis with pure water and with 0.05 n NaOH at 130, 150 and 170°C and time periods of 10, 30 and 60 min at each temperature and with each solvolysis medium. Figure 6 shows the hexogen yields both graphically and in numerical form. The yield decreases with increasing alkalinity,

TABLE 2
Characterisation of GAP and the GAP Samples Solvolyzed at 170°C using IR-absorption DSC and GPC

Solvolytic medium	Solvolytic time (h)	N ₃ -group content IR (%)	N ₃ -group content DSC (%)	Molar masses in g·mol ⁻¹ from GPC			
				Mn	Mw	Mz	Mmax
—	—	100	100	2940	3500	4320	3140
n-heptane	2	88	89	2840	4200	6930	2930
Touene	1	98	98	2910	3830	5470	3040
Toluene	2	80	81	2990	4180	6410	2960
Water	1	90	92	2850	4000	6260	2980
Water	2	80	82	2710	4210	7340	2790
Water	2	84	84	2570	4140	7270	2790
0.05 n NaOH	2	30	33	2630	3610	5310	2850

TABLE 3
Generated Gases during the Solvolyses of GAP and of Cured Binder GAP-N100

Sample	Solvolytic medium	Solvolytic time (h)	Solvolytic temp. (°C)	Gases in ml (at 20°C, 1 atm) per g sample					
				N ₂	N ₂ O	O ₂	CO	CO ₂	NO _x
GAP	Water	2	170	10.2	0.61	0.68	0.02	0.24	0.21
GAP	0.05 n NaOH	2	170	4.43	0.15	0.18	—	—	0.0004
GAP-N100	0.05 n NaOH	1	170	3.96	0.02	0.79	—	—	0.0003

solvolytic time and solvolysis temperature. Already a hydrolysis lasting for 10 min at 130°C permits to recover up to more than 95% of the hexogen used in this gun propellant formulation. Using DSC and melting point determination, the purity of the hexogen was demonstrated, and the agreement of the melting point with that of the hexogen initially used was found to be very good. There was always a binder residue present, for the reasons already discussed in Section 6.3.

Gas was formed in all solvolyses of the gun propellant (GP) KHP. Figure 7 shows the gas volumes determined. The main component was N₂, followed by N₂O, CO₂, O₂ and CO. For both solvolytic

agents, the gas quantities for the individual components are given per g KHP for a solvolysis at 170°C lasting for 1 h in Fig. 8. In the case of KHP, the binder content is only 14 mass%. Corresponding to the data in Table 3 for the GAP solvolysis, it can be recognized that the main quantities of gaseous products arise from the decomposition of hexogen. The total amount of gases produced at 130°C and 10 min solvolysis time in water is very low, 1.6 ml per g KHP.

For some solvolyses a summary of the ionic reaction products: nitrite NO₂⁻, nitrate NO₃⁻, and ammonium NH₄⁺ is given in Table 4. The decomposition of hexogen produces formate also.⁸ In the

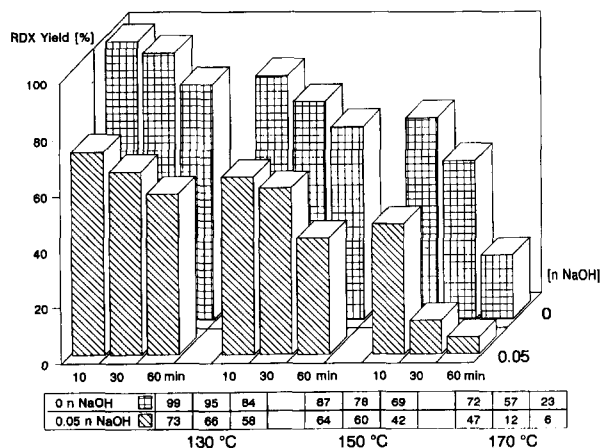


FIGURE 6. Yield of RDX in the solvolyses of the GP KHP.

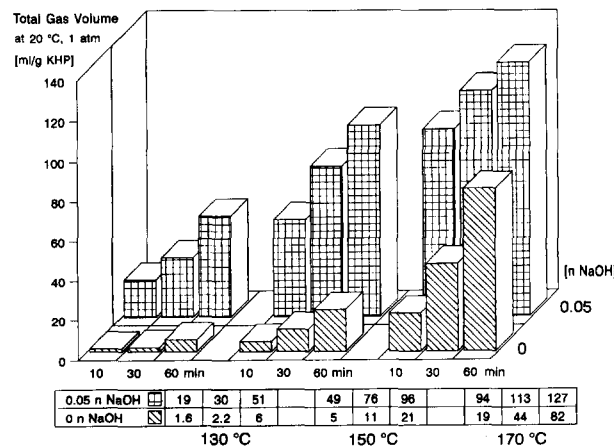


FIGURE 7. Generated total amounts of gas during the solvolyses of the GP KHP in ml per g KHP.

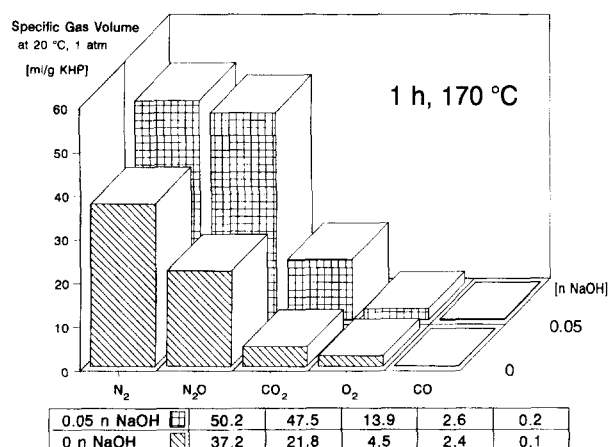


FIGURE 8. Main components of the gas formation in the solvolyses of GP KHP at 170°C and 1 h in ml per g KHP.

literature,^{9,14} (see Section 6.5.2), the formation of formaldehyde CH_2O and ammonia NH_3 was found by aqueous alkaline hydrolysis. These two substances were not analysed here but were probably formed. The mentioned reference quotes nothing about the formation of nitrate, which was here found in considerable quantities. The conditions of investigation in that work were, however, different ones; 25, 35 and 45°C, and only minor concentrations of RDX dissolved in water.

A second gun propellant, named KHP RG2, with nearly the same composition as the above KHP was solvolysed in the same manner with pure water.⁸ The results on the RDX yield are similar. The binder of KHP RG2 was somewhat more tight, so the yield passes at each temperature a maximum as function of time (Fig. 9) where the KHP is named KHP RG1.

6.5 Decomposition Mechanisms for Hexogen

As solvolysis is carried out at relatively high temperatures, we should also take into account thermal decomposition. From the adiabatic self-heating, measured with an "Accelerating Rate Calorimeter" (ARC[®], Columbia Scientific Industries, U.S.A.),¹⁰ one can conclude a thermally initiated decomposition already below 180°C. In diluted solutions of RDX in cyclohexanone the start of the decomposition determined with the ARC is already at 120°C.

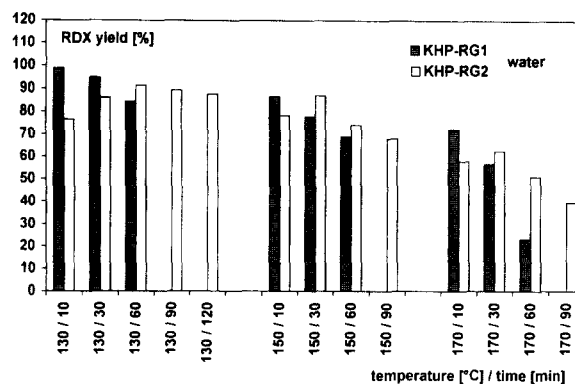


FIGURE 9. RDX yield in the solvolyses of the two gun propellants KHP = KHP RG1 and KHP RG2.

6.5.1 Thermal decomposition of hexogen. The thermal decomposition of hexogen and its kinetic-mechanistic determination is complicated, has been investigated many times, and is still a subject of research. The reaction products of the decomposition reaction were determined in a temperature range between 180 and 300°C. These vary somewhat quantitatively as well as qualitatively, according to the test design selected, and very probably also to the analytical ability.

One of the earlier comprehensive studies is that by Robertson.¹¹ He investigated the decomposition of RDX in a temperature range between 213 and 299°C with quantities between 4 mg and 45 mg, and found the following reaction products (in mol/mol RDX): N_2 (1.16), N_2O (0.98), NO (0.54), CO_2 (0.48), CO (0.40), H_2 (0.09), and not quantified CH_2O and H_2O . He was not able to demonstrate the presence of any NO_2 , NH_3 or HCN .

Rauch and Fanelli¹² found additionally HCN , were able to demonstrate NO_2 in the gaseous phase decomposition, but do not indicate any N_2 .

Batten¹³ discovered that CH_2O accelerates the decomposition of RDX in the solid and liquid phase. NO_2 has a retarding effect, which is attributed to the reaction of the NO_2 with CH_2O and thus its elimination.

Cosgrove and Owen¹⁴ attempted to cover the entire product spectrum. At 195°C, they found the following reaction products (in mol/mol RDX): N_2

TABLE 4
Ionic Reaction Products from some Solvolyses at 170°C

Sample	Solvolysis medium	Solvolysis time (h)	Ions in mg per g sample		
			NO_2^-	NO_3^-	NH_4^-
GAP	Water	2	--	—	4.0
KHP	Water	1	—	89.1	—
KHP	0.05n NaOH	0.5	0.7	38.9	2.8
KHP	0.05n NaOH	1	1.0	149.3	5.0
Hexogen	0.05n NaOH	1	1.2	344.2	12.7

(1.26), N₂O (1.08), NO (0.51), CO₂ (0.70), CO (0.36), CH₂O (1.04), HCOOH (0.37), NH₃ (0.34), NO₃⁻ (0.1) and NO₂⁻ (0.02). As decomposition residue, they identified N-hydroxy-N-methyl formamide. These authors also found that CH₂O promotes the decomposition of RDX. In their arrangement of investigation, the decomposition in the gaseous phase predominated.

Hofsommer and Glover^{15,8} investigated the decomposition of RDX in benzene and D6-benzene between 180°C and 200°C and in the melt at 210°C. In the benzolic solutions, RDX decreased according to a reaction of first order, in the melt according to a reaction of zero order. In the rate determining step they identified N-nitroso-“RDX”, a NO₂-group in RDX is replaced by a NO group. The N-NO group was produced after proton abstraction from the solvent benzene with a consecutive splitting-off of an OH group from the N-NO₂ group.

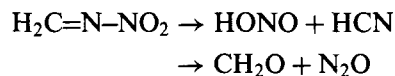
Pfeil, Krause and Eisenreich¹⁶ investigated the thermal RDX decomposition at three very different heating rates: the analysis of the gas production at approx. 5°C min⁻¹ heat rate with IR spectroscopy, burning in the optical bomb at 10⁵ to 10⁶°C min⁻¹ with UV-VIS analysis of the flame reaction products NH, CH, OH and CHO/CH₂O and with laser impulse heating at approx. 10¹¹°C min⁻¹ heat rate with time of flight mass spectrometric analysis of the pyrolysis products. They found NO, H₂CN, CN, HCN and ring fragments such as H-C-N, N-CH₂-N, N-CH₂-N-CH₂ and N-CH₂-N-CH₂-N, their size depending on the pulse energy. It is assumed that the ring fragments split-off NO₂ rapidly. The following reaction products were found at the slow thermal decomposition with 5°C min⁻¹ heat rate: N₂O, CH₂O, HCN, NO, CO₂, CO, H₂O, CH₃OH and NH₃. With IR it was not possible to detect any N₂, which probably may have formed. From the development of the reaction products with time, the authors concluded that N₂O, CH₂O and HCN are primary reaction products. That means, NO and CO₂ as well as the other products are produced via reactions from or between the reaction products, presumably under participation of NO₂. These results allow to conclude the existence of a C-N bond breaking as main reaction on slow decomposition. On rapid heating up, the RDX molecule breaks down isolated in the gaseous phase, so that an N-N bond breaking and the splitting-off of NO₂ here belong to the primary reaction steps. The C-N bond break predominates in the condensed phase.

Behrens and Bulusu¹⁷ established a schematic presentation of the main decomposition paths, deduced from the existing results:

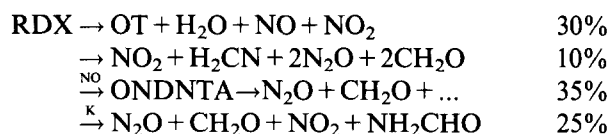
- N-N bond splitting with formation of NO₂
RDX → NO₂ + H₂C=N | +2H₂C=N-NO₂

- concerted triple splitting
RDX → 3H₂C=N-NO₂
- HONO elimination
RDX → 3HONO + 3HCN

The methylene nitramine can break down in two ways:



In the crystalline phase, RDX decomposes slowly, but much more rapidly in the liquid phase or in the melt. The authors found the following reaction products (no conversion data are given): N₂O, CH₂O, NO, CO, HCN, H₂O, NO₂, HONO, NH₂CHO, CH₃-NH-CHO, oxytriazine (OT), and 1-nitroso-3,5-dinitrohexahydro-triazine (ONDNTA=N-NO-“RDX”). In their reaction design in a special TGA-MS apparatus, no N₂ was found, and also no NH₃, HCOOH and CO₂. In the context of their results, they give the following four decomposition paths with a corresponding occurrence probability:



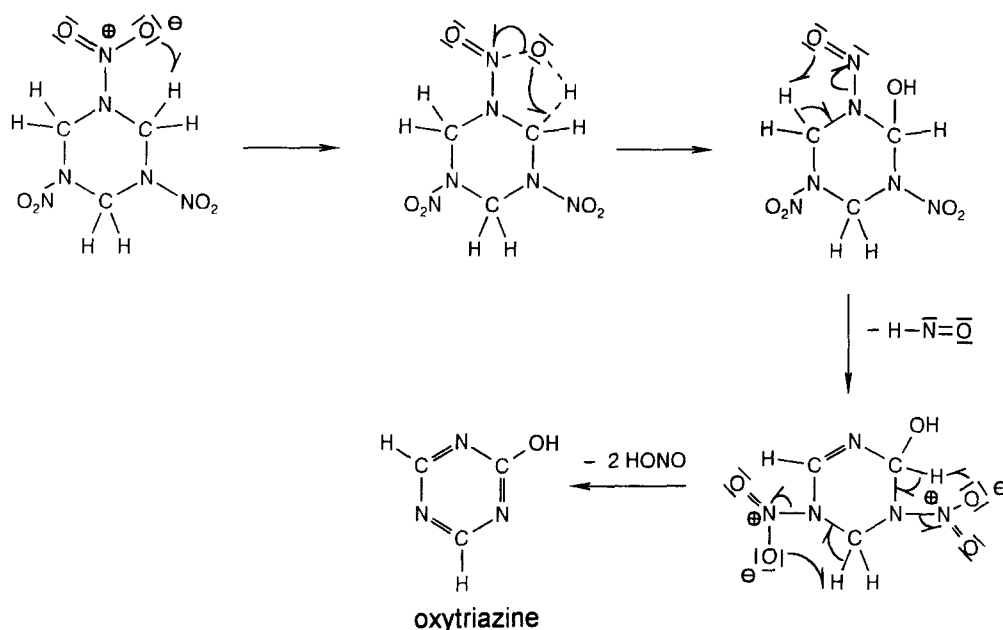
K is a catalyst from the product spectrum, which was not specified further. The formation of the product oxytriazine is shown in Fig. 10. The reaction paths leading to its formation were concluded from the result of an isotope labeling. The authors conclude that ONDNTA is formed by splitting-off a NO₂ radical from RDX and subsequent addition of a NO radical.

6.5.2 Decomposition of hexogen in aqueous solutions. The product spectrum of the decomposition of hexogen in aqueous and alkaline hydrolysis is similar to that in thermal decomposition. Here however, the formation of ionic products is markedly pronounced.

In 1940, Somlo¹⁸ found, in the alkaline hydrolysis of RDX at 60°C in 1 n NaOH, the following reaction products per mol converted hexogen:

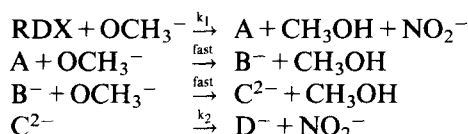
- 0.8 mol of NO₃⁻ and NO₂⁻, as sum
- 3.5 mol acids, of which 2.7 mol are organic acids, he assumed HCOOH,
- 0.88 mol NH₃,
- 1.89 mol N₂
- and non-quantified formaldehyde.

Epstein and Winkler¹⁹ carried out an alkaline hydrolysis at 0 and 15.5°C in acetic solution. Their

FIGURE 10. Decomposition path of RDX to oxytriazine.¹⁶

RDX was rapidly decomposed, they indicated no reaction products.

Jones²⁰ investigated the reaction of RDX between 19°C and nearly 45°C in methanolic solution with CH₃OH/KOH, CH₃ONa and CH₃OLi. From his results, he established the following reaction scheme:



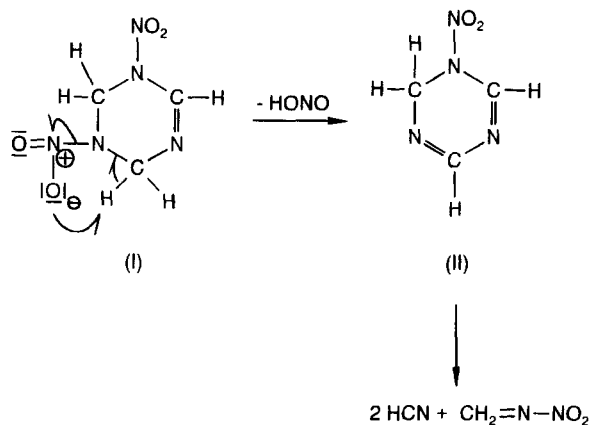
The reaction rate constants k_1 and k_2 have the following Eyring parameters:

	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	Δn^\ddagger (mol)	E_a (kJ mol ⁻¹)
k_1	116.7	98.7	-1	121.7
k_2	92	-33	1	92

A detailed investigation was carried out by Hoff-sommer *et al.*¹⁴ at 25, 35 and 45°C using 0.02 n to 0.25 n NaOH. For their mechanistic interpretation, they also used deuterated RDX. These authors found the following hydrolysis products (in mol/mol RDX): NO₂⁻ (1.1), N₂O (1.2), CH₂O (1.1), N₂ (0.12), NH₃ (0.9) and HCOO⁻ (0.7). The following were not found: NO₃⁻, CO, CO₂, NO, NO₂ and O₂. From the H/D-kinetic isotope effect they concluded a separation of H⁺ from a methylene group of the RDX through OH⁻ as a first reaction step, connected with the concerted splitting-off of a nitrite ion. 1,3,5-triaza-3,5-dinitrocylohexene-1 is formed (Fig. 11 (I)). This reaction step had also been sup-

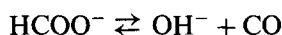
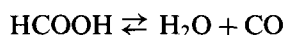
posed by Jones.²⁰ The presence of the product (I) was not definitively demonstrated by Hoff-sommer *et al.*,¹⁴ it was only deduced. It is assumed that a further molecule, HONO, is eliminated in a fast reaction, and that this product (II) (Fig. 11) is hydrolyzed further. This is a similar path as in the formation of oxytriazine (Fig. 10). The authors isolated a hydrolysis product and assumed the presence of (I), although they were only able to demonstrate (II)

6.5.3 Interpretation of the spectrum of decomposition products from the solvolyses of the KHP. The -N=CH- groups in the hydrolysis products (I) or (II) are converted into HCN and this further hydrolyzes into HCOOH and NH₃, under the solvolytic conditions applied here, whereby a way to these reaction products is then opened. The ring break-down may

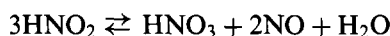
FIGURE 11. Decomposition of RDX after the concerted (NO₂⁻-H⁺) splitting-off by the attack of OH⁻ at a methylene group of RDX, formation of H₂O and NO₂⁻.¹⁴

be also a concerted reaction with the hydrolysis of HCN. After the separation of the two HCN groups in (II), the methylene nitramine can then decompose into CH_2O and N_2O , Fig. 12, but the path to HCN and HONO is possible also. From the product spectrum of the KHP solvolysis one can conclude that, in the aqueous phase, the formation of CH_2O and N_2O is predominant, as a relatively marked formation of N_2O was found.

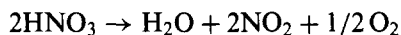
The decomposition reactions given up to now do not explain the reaction products CO_2 , CO , N_2 , O_2 and NO_3^- . Possible formation paths are consecutive reactions of decomposition products and reactions between the decomposition products. Formic acid can decompose into H_2O and CO :



Nitrite is formed in larger quantities. As the pH value decreases during solvolysis by consumption of the OH^- , the nitrous acid is able to disproportionate:



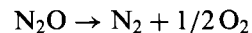
This explains the occurrence of NO_3^- and in part the low concentrations of NO_2^- in the hydrolysates obtained. Under these conditions, the NO itself can react back to HNO_2 , as the solvolyses are carried out in a helium atmosphere. A possible source for O_2 would be the decomposition of HNO_3 :



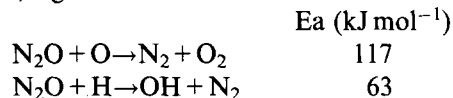
The NO_2 formed by this reaction can oxidize CO to CO_2 and CH_2O to HCOOH .

At the temperatures at which the solvolytic processes have been performed, N_2O is thermodynamically

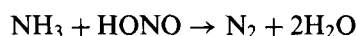
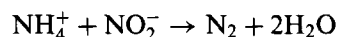
unstable, the decomposition reaction is however inhibited by the medium-high activation energy of approx. 250 kJ mol^{-1} .



However, there are reactions with lower activation energies, e.g.:²¹



For nitrogen as a reaction product, a possible formation path under these reaction conditions is that NH_4^+ and NO_2^- react to form N_2 and H_2O :



This path reduces both NO_2^- as well as NH_3 or NH_4^+ in the reaction spectrum, which has been found in further studies also.

7. SUMMARY

The recovery of polyetherpolyols and ammonium perchlorate (AP) from a model solid propellant (FTS) with 60 mass% AP and of hexogen and GAP from the solid gun propellant KHP was investigated via solvolysis with pure water and alkaline water (0.05 n to 0.5 n NaOH) between 130 and 170°C. The FTS binder manufactured from the polyetherdiol Lupranol 1000 and the polyethertriol Lupranol 2021 and the curing agent Desmodur T80 is solvolytically easy to decompose, the polyols can be recovered up to and above 90% yield. The released AP content was determined using ion chromatography, and was at 98%. The Lupranols were nearly not changed,

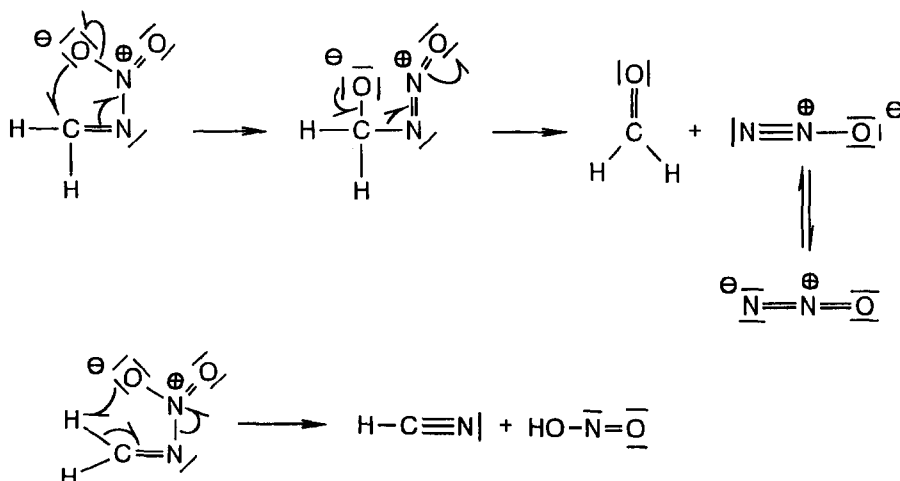


FIGURE 12. Decomposition channels of methylene nitramine $\text{CH}_2=\text{N}-\text{NO}_2$: formation of CH_2O and N_2O or HCN and HNO_2 .¹⁷

even when exposed to extreme solvolytic conditions, i.e. 170°C at 2 h, as the comparison of the molar mass distributions (MMD) between the unexposed and the recovered polyols show.

GAP is also a polyetherdiol, formally on the basis of propane-1,2-diol with azide groups. A GAP binder ought to behave solvolytically in the same way as a Lupranol binder. This is not the case. Through the splitting-off of nitrogen from the N₃-group, the highly reactive nitrene thus formed produces C–N-bonds, which are solvolytically not scissionable. The decrease in N₃-group content through solvolytic exposure was determined via infrared absorption of the asymmetric N₃ stretching vibration and via the decrease of its energy content determined with DSC. In pure water at 170°C, the N₃-group content decreases by approx. 9 to 10% after 1 h and 18% after 2 h. The MMD of the solvolyzed GAP samples became lower and broader, the higher molecular portion increased markedly.

The KHP was solvolyzed with pure water and 0.05 n NaOH at 130, 150 and 170°C, with solvolysis times of 10, 30 and 60 min at each temperature and with each solvolysis medium. With increasing alkalinity, increasing time and increasing temperature of solvolysis, the yield of hexogen decreases. Ten minutes of hydrolysis at 130°C already allow to recover over 95% of the hexogen in this KHP formulation. The purity of the recovered RDX was high, as the equality of its melting point with that of the hexogen used in manufacturing the KHP showed. The recovery of the GAP was not possible.

In all solvolytic processes involving KHP, gases and ions were formed as decomposition products. As regards the gases, N₂ was the major component followed by N₂O and additionally some CO₂, O₂ and CO. The gases NH₃ and CH₂O were not quantified. The ionic products are NO₂⁻, NO₃⁻, HCOO⁻ and NH₄⁺. From the investigations on the decomposition behavior of hexogen both thermally, in solution with organic solvents and also in aqueous, alkaline solutions, one can conclude that N₂, O₂, CO, CO₂, HCOOH and NH₃ are formed by reactions between the decomposition products and by reactions with the solvolytic agent.

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