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THE POLYMERIZATION OF HIGHER DIAZOALKANES*

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THE polymerization of aliphatic diazo compounds (diazoalkanes) is at present almost the only method of synthesizing carbon-chain polymers with alkyl substituents on every C-atom of the main chain. One of the still unsolved questions of this method is the synthesis of higher polyalkylidenes (from polypentylidene upwards). Numerous attempts were made to produce them [1, 2], but all in vain. An interesting point noted was that only diethyl ether had been used as solvent in these experiments. The special structure of the alkyldiazomethane mole-

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cules, containing a polar and an easily polarized diazo group, as well as a non-polar alkyl substituent, led to the assumption that the nature of the solvent could seriously affect the reaction.

The influence of the solvent on the aliphatic diazo compound polymerization had not been so far the subject of a systematic study. Diethyl ether is normally used as solvent. The alkyldiazomethanes (up to and inclusive of diazobutane) are shown to form polyalkylidenes in the ether when various catalysts (BX_3, X being halogen, alkyl, aryl, alkoxyl [1, 3, 4]; copper and its salts [1, 2, 5], gold and a number of other metals [6]) were present. The decomposition of higher diazoalkanes in ether over metallic copper, or Cu-stearate gives chiefly rise to the respective azines and alkene dimers with a central double bond [1, 2].

Where unsaturated hydrocarbons are used as solvents, the lower diazoalkanes form polymers over a BX_3-type catalyst (our findings) and gold [6]. Copper and its salts will cause the diazoalkanes to decompose in these solvents, and to yield only low mol. wt. products [2, 6]. An interesting point is that the diazo-ethane decomposition over the copper foil in a diethyl ether-pentane mixture yielded polyethylidene in quantities proportional to the diethyl ether content [7].

The above findings permit the assumption of the solvent–catalyst combination being a very sensitive, and sometimes even the decisive factor, in the catalytic decomposition of diazoalkanes. It would have been interesting, with this in mind, to study the decomposition of higher diazoalkanes in different solvents (saturated hydrocarbons, ether, tetrahydrofuran, and their mixtures), and over different types of catalysts.

We selected the most typical from amongst the catalysts, i.e. BF_3·diethyl etherate and copper stearate, in the decomposition study of diazohexane. The gold catalyst was a stable, and storable solid, the $AuCl_3$–pyridine complex [8]. Preliminary tests showed this catalyst to be easily reduced during reactions with the solutions of diazoalkanes, such as diazomethane, diazoethane, diazobutane at -10 to $+20$°C in various solvents, and to form finely disperse metallic gold.

Judging from the decomposition rate of the diazoalkanes, and from the polymer yield, the polymerization of diazomethane and diazoethane over $AuCl_3 \cdot C_5H_5N$ took a course similar to that described by Nasini *et al.* [6] for the polymerization of the same diazoalkanes over $AuCl_3$. A series of parallel tests of diazohexane decomposition in octane at room temperature over Cu-stearate, BF_3·etherate and the $AuCl_3$–pyridine complex showed these catalysts to behave differently in the conditions studied.

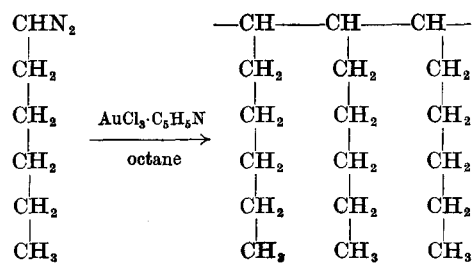
The BF_3·etherate caused a slow diazohexane decomposition (several days) and the result were mainly low mol. wt. products, and polymer traces. The copper stearate decomposed the diazohexane more quickly; the colour of the solution faded in 1–2 hr, but no polymer was found amongst the decomposition products.

The copper sterate decomposed the diazohexane more rapidly; the solution lost its colour in 1–2 hr, but there was no polymer amongst the decomposition products. $AuCl_3 \cdot C_5H_5N$ also decomposed the compound in a few hours. The composition of the reaction products was quite different from that obtained in the presence of BF_3-etherate and copper stearate. Polyhexylidene was obtained for

TABLE 1. SYNTHESIS OF HIGHER POLYALKYLIDENES

Diazoalkane	Concentration, mole/l.	Catalyst, ml/l.	Polymer yield, % theor.	Chain unit	Elemental analysis, %			Mol. wt.	Polymerization coefficient
					element	calculated	found		
Diazopentane	0·23	125	25	$-CH-$ C_4H_9	C	85·61	85·70 85·82	3500±300	50±5
					H	14·39	14·53 14·70		
Diazohexane	0·18	250	57	$-CH-$ C_5H_{11}	C	85·61	85·53 85·83	7000±700	80±8
					H	14·39	14·18 14·20		
Diazoheptane	0·15	200	68	$-CH-$ C_6H_{13}	C	85·61	85·00 85·09	7500±800	75±7
					H	14·39	14·11 14·10		
Diazooctane	0·10	150	19	$-CH-$ C_7H_{15}	C	85·61	85·20 85·32	8500±900	70±7
					H	14·39	14·14 14·00		

the first time when diazohexane was decomposed in octane as solvent over the Au-containing catalyst:



The polyhexylidene yield was 40–60% of theoretical in the studied conditions; the mol. wt. varied from 3·5 to 6·5 $\times 10^3$ (gaseous osmometry, chloroform as solvent).

The method developed for the diazohexane polymerization was extended to higher diazoalkanes. Using normal diazopentane, diazoheptane and diazooctane, we produced other polyalkylidenes of general formula $\left[\begin{array}{c}-CH-\\ |\\ C_nH_{2n+1}\end{array}\right]_m$ for the first time, i.e. polypentylidene, polyheptylidene and polyoctylidene.

The structures of the higher polyalkylidenes was confirmed by elemental analysis (see Table 1) and by infrared spectroscopy. The polymer yield varied from 20 to 60–70% of theoretical; the mol. wts. were usually in the range $3{\cdot}5–8{\cdot}0 \times 10^3$ (polymerization factor 40–80).

The higher polyalkylidenes synthesized over $AuCl_3 \cdot C_5H_5N$ were either plastics (polyamylidene, polyhexylidene, polyheptylidene) or highly viscous resins (polyoctylidene), and were pigmented by the finely disperse metallic gold to a lilac-pink colour which normally faded on repeated precipitation. These polymers had good solubility in the majority of organic solvents (ether, chloroform, aromatic and saturated hydrocarbons), and were precipitated from them with methanol or ethanol.

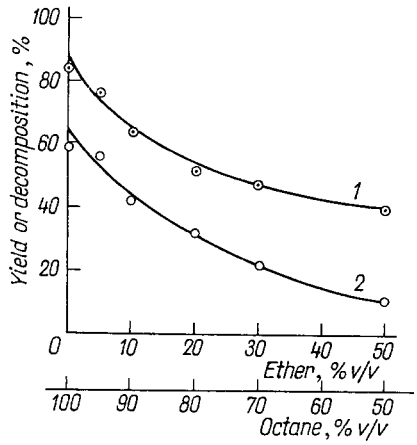


FIG. 1. Polyhexylidene yield (% theor.) and diazohexane decomposition for 12 hr (as % of original diazohexane) as a function of solvent composition: *1* — % diazohexane decomposition, *2* — polyhexylidene yield.

The production conditions of the higher polyalkylidenes, and some of their properties, are listed in Table 1. Thus, diazomethane gave a quantitative yield of polymethylene over finely disperse gold in ether as solvent [6], diazoethane a 30–35% polymer yield [9], diazopropane and diazobutane an about 10% yield [6], and diazohexane only traces of polymer. The diazohexane decomposition over the same catalyst in octane, however, produced a 40–60% polyhexylidene yield.

The following factors are thought to affect the mechanism of solvent effect on the diazoalkanes decomposition in the presence of $AuCl_3 \cdot C_5H_5N$:

(1) different electron densities on the diazo C-atom of the diazoalkane molecules; these are associated with changes in the size of the alkyl substituents and result in a different adsorption tendency on the surface of metallic gold;

(2) steric hindrance when polymerizing higher diazoalkanes, which is more pronounced in ether as solvent;

(3) the rate of formation and the size of the metallic gold particles produced in the presence of diazoalkanes from the original Au-containing substance.

To verify the latter assumption, we made a series of diazohexane decomposition tests by adding $AuCl_3 \cdot C_5H_5N$ in octane/diethyl ether mixtures of different composition. These tests showed that a larger proportion of the ether present in the mixture led to a finer dispersion of the forming metallic gold, judging from the colour of the reaction mixture and the sedimentation rate of the gold particles (this fact agrees well with the results reported by Ledwith [10], who reduced $AuCl_3$ with aliphatic diazo compounds in different solvents). The surface enlargement of the catalyst by the ether addition should thus accelerate the catalytic decomposition of the diazoalkane. The reverse was in fact observed in the tests (Fig. 1). The larger the ether content of the solvent mixture, the smaller was the rate of diazohexane decomposition and the polyhexylidene yield. The effect of the solvent type on the polymerization must therefore be due to other factors.

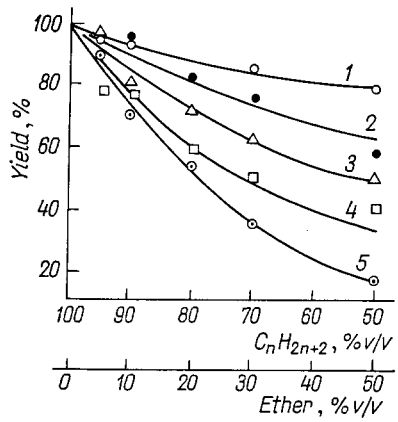


FIG. 2

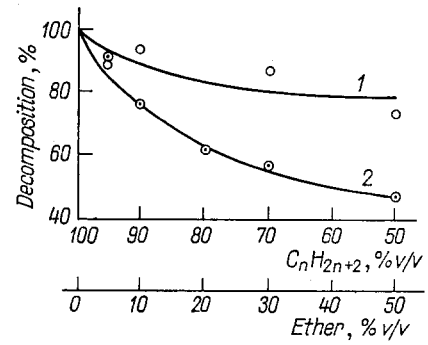


FIG. 3

FIG. 2. Polyalkylidene yields (as % of compound in the medium) as a function of solvent composition: *1*—polyethylidene, *2*—polypropylidene, *3*—polybutylidene, *4*—polypentylidene *5*—polyhexylidene.

FIG. 3. Conversion efficiency of (*1*) diazoethane and (*2*) diazohexane (as % decomposition of the diazoalkane in hydrocarbon solvent in the same period) as a function of solvent composition.

We made a series of decomposition tests with diazoethane, n-diazopropane, n-diazobutane, n-diazopentane and n-diazohexane by adding $AuCl_3 \cdot C_5H_5N$ in a solvent mixture made up of a saturated hydrocarbon and diethyl ether, these

ingredients being taken in different ratios (from the pure hydrocarbon to a 1 : 1 alkane : ether mixture), to assess the probability of an influence of electron and steric factors. The rate of diazoalkane decomposition and the polymer yield was determined in each experiment within a series. The effect of solvent composition on the decomposition rate was assessed at the moment of it reaching 80–90% in the pure hydrocarbon as solvent.

The results of the above tests were compared with those obtained when decomposing the particular diazoalkane in a 100% hydrocarbon solvent.

Figure 2 shows the polyalkylidene yields plotted against the solvent mixture composition. A larger diethyl ether content can be seen to result always in a smaller polyalkylidene yield; this effect is all the stronger where a longer alkyl substituent R is present in the $R-\bar{C}H-N\equiv N$ molecule. For instance, the change from a hydrocarbon medium to a 50% alkane+50% ether mixture reduced the yield from 30 to 24% of theoretical. The reduction in the case of polyhexylidene was from 60 to 10% (by a factor of 6).

A similar tendency was observed in the plot of solvent composition against the rate of decomposition of different diazoalkanes (Fig. 3). The reasons for the latter not being as marked are thought to be the different weight to surface ratios of the metallic gold produced and the differing compositions of the decomposition products, which were functions of the solvent properties and of the diazoalkane structure.

The correlations shown in Figs. 2 and 3 lead to the conclusion that the electron density present on the diazo C-atom is not the decisive factor. Its gradual increase with increasing length of the alkyl substituent (enlargement of the induction effect) should have resulted in a more successful competition of the diazoalkane molecule with that of the ether for the catalyst surface. The opposite tendency was, in fact, observed. The polymerization-hindering effect of the ether seems to be chiefly due to a steric factor.

The replacement of the ether by the more polar tetrahydrofuran (THF), which is also a better solvent, hindered still more the polymerization of the higher diazoalkanes and also reduced the decomposition rate of the diazo compound (Fig. 4), as well as the polymer yield (Fig. 5). It appears that these properties, i.e. the polarity and solvating capacity, hinder the polymerization.

We believe the mechanism of this phenomenon to be connected with the structural features of the diazoalkanes, namely the presence of a low polarity hydrocarbon radical and a polar diazo group in a single molecule. The polar diazo groups are dissolved by the solvent molecules in ether and particularly in THF, while the diazoalkane molecules are randomly distributed throughout the bulk of the solvent. This reduces the polymerizing capacity of the diazoalkanes fairly quickly, and also the screening capacity of the alkyl substituent.

Where the diazoalkanes are present in saturated hydrocarbons having low polarity, which also are poor solvents, the energy for a reaction between the polar diazo groups is undoubtedly greater than that with the solvent molecules. This

creates conditions for the appearance of lyophobic reactions [10] which can lead to a certain steric organization of the diazoalkane molecules, and could reduce the steric hindrance by the hydrocarbon radicals. This state then makes possible the polymer formation.

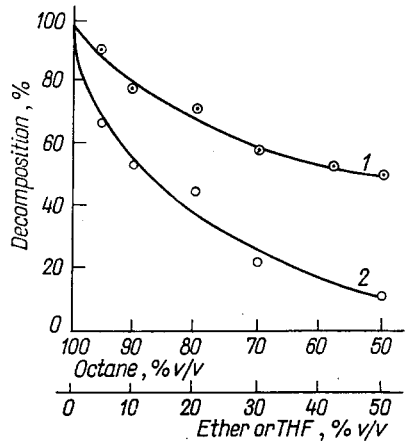


FIG. 4

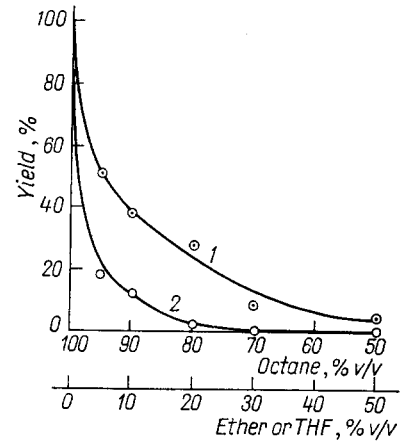


FIG. 5

FIG. 4. Diazohexane conversion efficiency (as % of that in octane in the same time) as a function of solvent composition: *1*—with a diethyl ether addition; *2*—with a THF addition

FIG. 5. Polyhexylidene yields (as % of its yield in octane) as a function of solvent composition. *1* and *2* as in Fig. 4.

The authors wish to express their gratitude to B. L. Yerusalimskii and V. A. Kabanov for valuable criticism.

EXPERIMENTAL

a) *N-nitroso-N-alkylurea* (*NAU*) was produced by heating the respective primary amines with a 4–6 fold excess of urea in a slightly acid solution (as described for the synthesis of methyl- [12] and propyl- [13] urea). The completion of the reaction left the NAU R—NH—CO—NH_2, in which R=CH_3, C_2H_5 or C_3H_7, in the solution, so that it could be nitrosated without prior extraction [12, 13]. Where the NAU had R=C_4H_9 or higher, the solubility was much poorer and it had to be extracted prior to nitrosation in cooled acetate solution (as described in [14]). The NAU yields and some of their properties are listed in Table 2.

b) Diazoethane, n-diazopropane, n-diazobutane, n-diazopentane, n-diazohexane, n-diazoheptane and n-diazooctane were all produced as solutions by the Arndt method [14], i.e. by alkaline cleavage of the respective NAU. The solvents were saturated hydrocarbons and were selected because they had similar vapour pressures to those of the particular diazoalkane (Table 3). The solutions of the latter were freeze-dried at −40 to −70°C, followed by filtration in an argon atmosphere and purification by recondensation. The diazoalkane concentrations were determined by titration with benzoic acid [16].

The diazoalkane solutions were normally used directly after their production and purification. Some characteristics of the above synthesis and purification of the solutions are contained in Table 3.

TABLE 2. PRODUCTION AND SOME OF THE PROPERTIES OF NÁU R—N(NO)—CO—NH_2

R	% Theor. yield *	N content, %		M.p., °C†	Some IR spectral lines, cm^{-1}‡		
		calculated	found		C=O	N—N=O (N=O)	N—N=O (N—N)
C_2H_5	50–60	35·88	35·01 34·89	96–98	1742	1500	–
n-C_3H_7	30–35	32·05	30·75 30·99	75–77	1740	1503	905
n-C_4H_9	30–35	28·95	28·45 28·67	81–82	1740	1502	920
n-C_5H_{11}	40–45	26·40	26·55 26·65	69–70	1740	1503	950
n-C_6H_{13}	50–55	24·26	24·66 24·77	70–72	1745	1504	975
n-C_7H_{15}	50–60	22·44	22·38 22·33	68–70	1745	1504	978
n-C_8H_{17}	60–65	20·88	19·93 20·14	66–69	1743	1503	996

* The yields given are based on the amine amount used in the first synthesis stage.
† The m. p. is that of thoroughly dried samples not subjected to the final purification.
‡ The samples used in the infrared spectroscopy were 0·5% solutions in CCl_4; the spectrometer DS-301 (Japan).

TABLE 3. SYNTHESIS OF ALIPHATIC DIAZO COMPOUNDS

Diazo-	Solvent	Recondensation temperature, °C at 1 mmHg	% Theoretical yield
Ethane	Petroleum ether, b.p. 40–60°	−20– −25	30–50
Propane	Ditto	−15– −20	35–50
Butane	Hexane	−10– −15	25–40
Pentane	Heptane	−5– −10	25–30
Hexane	Octane	0	25–30
Heptane	Ditto	0°–5	20–25
Octane	Octane + decane (2 : 1)	15–20	20–25

Catalyst preparation. The $AuCl_3 \cdot C_5H_5N$ complex was produced by reacting purified pyridine with an aqueous solutions of aurohydrochloric acid [8].

The copper stearate was produced by reacting copper sulphate with sodium stearate in an aqueous solution, then recrystallizing from benzene [17, 18]. The BF_3·diethyl etherate was distilled immediately before using it.

Diazohexane decomposition in a hydrocarbon with different catalysts present. Each of 3 ampoules placed at 19–20°C in a thermostat was filled with 1 g diazohexane in 25 ml

octane. To the first ampoule were added 16·5 mg copper stearate, 10 mg $AuCl_3 \cdot C_5H_5N$ to the second, and 1 drop BF_3·etherate to the third. The diazohexane decomposed in 1–2 hr when Cu- or Au-containing catalysts were present, but the decomposition took several days under the influence of BF_3·etherate. The contents of the first and second ampoules were filtered, the reaction mixture from the third was thoroughly washed with an aqueous sodium carbonate solution, and with water. The octane was evaporated and the residue dried at 100°C under 0·01 mmHg vacuum to constant weight. The first ampoule (Cu-stearate as catalyst) yielded 0·44 g of an oily matter, from which polyhexylidene could not be isolated. The second ampoule ($AuCl_3 \cdot C_5H_5N$ as catalyst) yielded 0·34 g of a highly viscous material (52·5% theoretical yield of polyhexylidene). This was precipitated twice from chloroform with methanol to give 0·25 g polyhexylidene; mol. wt. about 3000 (gas osmometry, chloroform).

The processing of the third ampoule contents (BF_3·etherate as catalyst) yielded altogether 0·03 g of an oil which appeared to consist of a low mol. wt. product mixture of diazohexane decomposition.

Synthesis of higher polyalkylidenes. To the solution of a higher diazoalkane in the appropriate solvent (Table 3), at 0–20°C, was added the $AuCl_3 \cdot C_5H_5N$ complex as catalyst. This compound was rapidly reduced by the diazoalkane under these conditions and formed a finely disperse metallic gold; subsequent decomposition was accompanied by the formation of nitrogen gas bubbles and a gradual fading of the solution colour. The polyalkylidenes were purified by 2–3 precipitations from chloroform with methanol. Completion of the diazoalkane decomposition (10–20 hr) was followed by the filtration of the solutions and vacuum-evaporation of the solvents. The results of some of the polyalkylidene syntheses by this method are contained in Table 1. The infrared spectra of the products confirmed their assumed structure.

Diazoalkane polymerization in hydrocarbon/diethyl ether and hydrocarbon/THF solvent mixtures of different composition, using $AuCl_3 \cdot C_5H_5N$ as catalyst. The diazoalkane solution (diazoethane to diazohexane) of 0·46–0·54 mole/l. concentration in the respective hydrocarbon solvent (Table 3) was equally divided over 6 ampoules. Each of these received identical volumes of the individual solvents, or of their mixtures. The diazoalkane solution thus prepared was reduced to 0·23–0·27 mole/l. and the solvent composition was varied from a 100% hydrocarbon to a mixture of 1 : 1 hydrocarbon : ether (or THF) by volume. The ampoules were placed in a thermostat and maintained throughout the experiment at 18–19°C. Each ampoule received an accurately weighed amount of $AuCl_3 \cdot C_5H_5N$ (125 mg/l.).

The diazoalkane decomposition was followed on samples taken periodically from the ampoule containing the pure hydrocarbon solvent, using titration with benzoic acid [16]. As soon as the decomposition amounted to 80–90%, the extent of the decomposition in all 6 ampoules was determined to evaluate the rate of decomposition as a function of medium composition. The ampoule contents, after completion of decomposition, were colourless or slightly coloured solutions, the colour being due to a fine dispersion of gold, while a black sediment, probably of metallic gold, was at the bottom. The solution was filtered and the solvent vacuum evaporated (the solutions in tests with diazopentane and diazohexane were washed several times, before vacuum evaporation, with dilute HCl to decompose any high-boiling azines present). The polymers remaining as residue were dried at 100°C/0·01 mm to constant weight.

The main decomposition products of diazohexane in an octane/THF mixture were high-boiling oily substances (apparently dodecene and lower oligomers). The polyhexylidene yields in this test series, and in the parallel one of diazohexane decomposition in octane/ether mixtures, were therefore determined after reprecipitation on equally dried samples under standard conditions (1 g of compound was dissolved after drying in 15 ml chloroform and precipitated with 150 ml methanol, the precipitate then separated and dried to constant weight).

CONCLUSIONS

(1) A method was developed for the production of higher polyalkylidenes; this consisted of a catalytic decomposition of the respective diazo compound in a saturated hydrocarbon by means of an $AuCl_3 \cdot C_5H_5N$ complex. The method developed was used to produce for the first time polypentylidene, polyhexylidene, polyheptylidene and polyoctylidene.

(2) Depending on the solvent properties (saturated hydrocarbons, diethyl ether, tetrahydrofuran, and their mixtures) the rate of the diazoalkane decomposition was found to vary and also the polyalkylidene yields. This effect was found to be the stronger with a longer alkyl substituent on the diazo carbon of the aliphatic diazo compound molecule.

(3) The polymerization possibility of higher diazoalkanes in a hydrocarbon medium was explained by the steric organization of the diazoalkane molecules, which are linked by a lyophobic interaction of the polar diazo groups in a solvent of low polarity, incapable of solvating them, and thus reducing steric hindrance

Translated by K. A. ALLEN

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