**Equilibrium Constants.**—The "apparent equilibrium constant" of the 1:1 and the 1:2 complexes in strongly basic solution may be determined from polarographic data for various ionic strengths. It may be seen by inspection of equation 12 that if we plot $(E_{1/2})_c - (E_{1/2})_s$ *vs.* log $[C_{GH_4^-} + p(i_d/2k_{GH_4^-})]^p (C_{OH^-})^x$, a straight line should be obtained whose slope is 0.0296 and whose intercept with the "*Y*" coördinate (at which the log term equals zero) is equal to 0.0296 log $K(k_s/k_c)$. The ratio $k_s/k_c$ is equal simply to the ratio of the diffusion currents $(i_d)_s/(i_d)_c$ measured for uncomplexed and complexed copper at the same concentration and ionic strength. Thus, $K$ determined in this fashion is not a true stability constant involving the formation of a complex directly from the metal and a ligand. It is the equilibrium constant for reaction 2a in which $p$ is given values of 1 and 2. It must be observed that this reaction included 2.5 hydroxide ions resulting in part from the dissociation of the second hydrogen ion of gluconic acid, for which the constant is unknown. We have calculated values of $K$ assuming the complex is a monomer, in order to facilitate comparison to stability constants of other chelates.

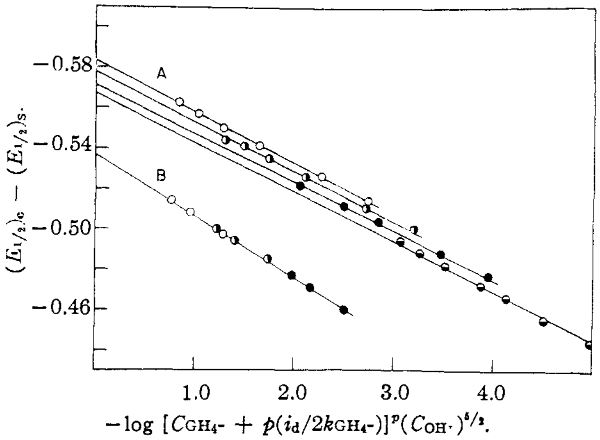

Fig. 4.—Determination of equilibrium constants: A, 1:2 complex ($p$ = 2); B, 1:1 complex ($p$ = 1) at various ionic strengths; ○, $\mu$ = 3 *M*; ◑, $\mu$ = 2 *M*; ●, $\mu$ = 1 *M*; ◒, $\mu$ = 0.45 *M*.

Figure 4 gives the plots used for the determination of equilibrium constants for the 1:1 complex (curve B) and the 1:2 complex (curve A). It will be noted that all experimental points for the 1:1 complex lie on one straight line with a slope of 0.031, indicating the equilibrium constant is independent of ionic strength in the region 1 to 3 *M*. However, the equilibrium constant for the 1:2 complex is dependent on the ionic strength since four straight lines with an average slope of 0.026 were obtained. The $pK$ ($-$log equilibrium constant) calculated for the 1:1 complex is 18.29. The $pK$ values calculated for the 1:2 complex at various ionic strengths at 25° are: $\mu$ = 3.0, 20.06; $\mu$ = 2.0, 19.85; $\mu$ = 1.0, 19.48; $\mu$ = 0.45, 19.43.

Los Angeles 24, California

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[Contribution from the Polymer Research Institute, Polytechnic Institute of Brooklyn]

# The Kinetics of the Catalyzed Decomposition of Diazohydrocarbons[1]

By Joseph Feltzin,[2] Alfred J. Restaino[3] and Robert B. Mesrobian

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Several polymeric hydrocarbons have been prepared by the catalyzed decomposition of diazomethane, diazoethane, diazobutane, and mixtures of the former two diazohydrocarbons. The kinetics of the decomposition reaction in ether catalyzed by cupric stearate or boron trifluoride have been studied. It is observed that the reaction rate is first order with respect to the diazohydrocarbon and the catalyst concentrations. The effect of catalyst and diazohydrocarbon concentrations on molecular weight was studied with the copolymer prepared from 80 mole per cent. diazomethane and 20 mole per cent. diazoethane. The molecular weight is found to be independent of diazohydrocarbon and catalyst concentrations. A polymerization mechanism involving propagation *via* a carbonium or diazonium ion and termination by interaction of growing chains with diazohydrocarbons is presented.

The decomposition of diazomethane to yield polymethylene was first reported by Bamberger and Tchirner.[4] Recent studies of this reaction have been concerned with the efficiency of various catalysts for conversion of diazohydrocarbon to polymer, the preparation of polyhydrocarbons from a homologous series of diazohydrocarbons,[5] and the physical properties of polymethylene derived from diazomethane.[6] This paper is concerned with the kinetics and mechanism of the catalyzed decomposition reaction in ether solution.

## Experimental

**Materials.**—Diethyl ether, U. S. P. grade, was used without further purification. Benzoic acid, toluene, hydroquinone, potassium cyanate, cupric sulfate and the various alkyl amines were reagent grade chemicals. Boron trifluoride etherate, trimethyl borate and tri-*n*-butyl borate were freshly distilled and diluted as necessary with ether. Cupric stearate was prepared by adding 6 g. of technical grade sodium stearate in 700 ml. of water to a 5% excess cupric sulfate solution. The precipitate was dissolved in ether and the solution filtered, concentrated to a small volume, and passed through a column containing 10 g. of activated alumina (Alcoa F-20 grade). The column was eluted with ether until the eluate appeared colorless. The eluate was filtered to remove traces of alumina, evaporated

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[2] Natvar Corporation (New Jersey) Fellow, 1951–1953. Abstracted in part from the dissertation of Joseph Feltzin, submitted in partial fulfillment of the requirements for the Ph.D. degree.

[3] Abstracted in part from the dissertation of Alfred J. Restaino, submitted in partial fulfillment of the requirements for the M.S. degree.

[4] E. Bamberger and F. Tchirner, *Ber.*, **33**, 956 (1900).

[5] (a) A. Loose, *J. prakt. Chem.*, **79**, 507 (1909); (b) K. Lorey, *ibid.*, **124**, 185 (1930); (c) H. Meerwein, *Angew. Chem.*, **A60**, 78 (1948); (d) G. D. Buckley, L. H. Cross and N. H Ray, *J. Chem. Soc.*, 2714 (1950); (e) *ibid.*, 3701 (1952); (f) L. C. Leitch, P. E. Gagnon and A. Cambron, *Can. J. Research*, **28b**, 256 (1950).

[6] S. W. Kantor and R. C. Osthoff, This Journal, **75**, 931 (1953).

to dryness and the residue stored *in vacuo* over calcium chloride; yield 8.3% based on converted sodium stearate. *Anal.* Calcd. for $C_{36}H_{70}O_4Cu$: C, 68.0; H, 11.00; Cu, 10.02. Found: C, 67.4; H, 10.33. Cu, 10.10. Analyses performed by the Schwarzkopf Laboratory.

$\alpha,\alpha$-Diphenyl-$\beta$-picrylhydrazyl was prepared by the method of Poirier, Kahler and Bennington.[7]

N-Nitroso-N-methylurea was prepared by the method of Arndt[8a] and used without recrystallization. The product was repeatedly washed with cold water until a sample was completely soluble in methanol at room temperature. N-Nitroso-N-ethylurea and N-nitroso-N-*n*-butylurea were prepared by the potassium cyanate method.[8b] These compounds also were used without recrystallization but were water washed until completely methanol soluble.

All ether solutions of diazohydrocarbons were prepared by the same method.[9] In a typical preparation 10 g. of N-nitroso-N-methylurea was added in small increments to a mixture of 50 ml. of 50% potassium hydroxide and 100 ml. of ether, with stirring and maintaining temperature in the range −10 to 0°. The ether solution of diazoethane was carefully decanted from the aqueous potassium hydroxide layer and used without further purification.

**Rate Measurements.**—The rates of decomposition in ether catalyzed by cupric stearate or boron trifluoride were determined by following the decrease in diazohydrocarbon concentration by titration with standardized benzoic acid.[10] In a typical experiment, 0.2 ml. of an ether solution containing 0.2 mg. of cupric stearate was added to 25 ml. of an ether solution of diazoethane of approximately 0.25 molar concentration. The solution was then poured into a water jacketed buret maintained at ±0.1° in the range 3 to 25°. Two-ml. aliquots of solution were withdrawn at varying intervals and added to a standardized excess of benzoic acid in toluene. Reaction of benzoic acid and diazohydrocarbon was instantaneous. The excess benzoic acid was back titrated with methanolic sodium hydroxide using *m*-cresol purple indicator.

**Preparation of Polymers.**—Solutions of diazohydrocarbon in ether of quantities sufficient to produce at least 0.5 g. of polymer were decomposed at a specified temperature by addition of catalyst. The resultant polymer was precipitated by addition of the ether solution to a 10-fold excess of methanol and the precipitate filtered and dried *in vacuo* at room temperature. The polymers and copolymers derived from diazomethane were ether insoluble and precipitated during reaction. These products were collected by filtration, washed with methanol, and dried *in vacuo*.

**Effect of Impurities on Decomposition Reaction.**—It was frequently observed that diazobutane and diazoethane prepared from the corresponding nitroso alkylurea which was not completely soluble in methanol decomposed readily in ether solution upon addition of catalyst but did not yield a polymeric product. In order to specify the influence of impurities on the decomposition of diazobutane catalyzed by cupric stearate the following experiments were performed. Ether solutions of diazobutane were prepared from two batches of N-nitroso-N-butylurea. The first batch of N-nitroso-N-butylurea had been repeatedly water washed and was completely soluble in methanol while the second batch had been washed only once with water and exhibited a faint turbidity on dissolution in methanol at room temperature. A portion of the diazobutane ether solution prepared from the latter batch of N-nitroso-N-butylurea was distilled[11] under reduced pressure and the middle fraction collected. It was observed that the conversion of decomposed diazobutane to polymer and the decomposition rate catalyzed by cupric stearate were identical between diazobutane obtained from the first batch of N-nitroso-N-butylurea and diazobutane purified by distillation. The undistilled diazobutane obtained from the second batch of N-nitroso-N-butylurea, however, decomposed approximately one-fourth as fast as the other samples and the conversion to polymer was reduced from 91 to 12%. Although the impurity has not been identified, these observations indicate that it may be removed from the diazohydrocarbon solution either by distillation of the diazohydrocarbon or by the use of a pure N-nitroso-N-alkylurea. In this work, the latter method was employed.

**Viscosity Measurements.**—Limiting viscosity numbers in toluene were determined from viscosity numbers at four or more polymer concentrations. An Ubbelohde dilution viscometer having a flow time of 120 seconds for toluene at 20° was employed.

**Turbidity Measurements.**—Weight average molecular weights of two polymer samples derived from a 4:1 molar mixture of diazomethane–diazoethane were determined at room temperature from turbidity measurements at four polymer concentrations below 1 g./100 ml. of toluene using a Brice–Phoenix photometer. The refractive index increment of the copolymer in toluene was measured with a Raleigh interferometer and found to be −0.1641 cm.$^3$/g.

## Experimental Results

**Dependence of Decomposition Rate on Concentration of Reactants.**—The decomposition of diazobutane at several initial concentrations is represented as a first order reaction in Fig. 1. At the temperature employed, the thermal rate of decomposition was negligible compared with the rates of decomposition catalyzed by cupric stearate. The decomposition of diazoethane, catalyzed by cupric stearate and the decomposition of diazomethane–diazoethane (4:1 molar mixture) catalyzed by boron trifluoride in ether also exhibited a well-defined first-order dependence of decomposition rate on diazohydrocarbon concentration. Figure 2 represents a first-order plot of the decomposition of a 4:1 molar mixture of diazomethane–diazoethane in ether catalyzed by varying amounts of boron trifluoride. Evaluation of the slopes of the various runs clearly demonstrates a first-order dependence of decomposition rate upon catalyst concentration. The decomposition of diazobutane and diazoethane catalyzed by cupric

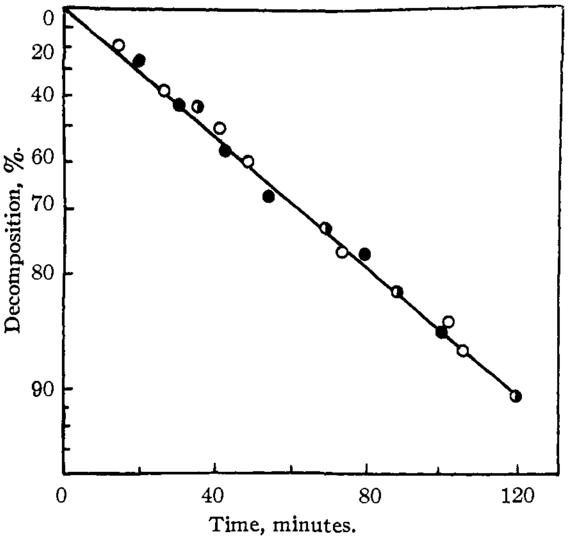

Fig. 1.—Decomposition of diazobutane in ether at 8° catalyzed by cupric stearate; dependence of rate on diazobutane concentration: ○, $C_4H_8N_2 = 0.146\ M$; ●, $C_4H_8N_2 = 0.353\ M$; ◑, $C_4H_8N_2 = 0.505\ M$; cupric stearate = $25 \times 10^{-6}\ M$.

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[7] R. H. Poirier, E. J. Kahler and F. Bennington, *J. Org. Chem.*, **17**, 1437 (1952).

[8] (a) F. Arndt, *Org. Syntheses*, **2**, 461 (1943); (b) F. Arndt, *ibid.*, **15**, 48 (1943).

[9] F. Arndt, *ibid.*, **2**, 165 (1943).

[10] Volumetric measurements of reaction rate were explored and found to be unsatisfactory due to supersaturation of liberated nitrogen gas in ether. This effect could only be overcome by rapid agitation of the hazardous diazohydrocarbon solutions.

[11] H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

TABLE I

DECOMPOSITION OF DIAZOHYDROCARBONS IN ETHER

| Reaction temp. °C. | $RCHN_2$, moles/l. | Catalyst | Catalyst concn., moles/l. | Conversion,[a] % | Appearance of polymer | $[\eta]^{20°}$ toluene, dcl./g. | $\bar{M}w$ |
|---|---|---|---|---|---|---|---|
| Runs with diazobutane | | | | | | | |
| 8 | 0.5 | Cupric stearate | $3.17 \times 10^{-6}$ | 92 | Glass | 0.10 | |
| 8 | .5 | Cupric stearate | $25.4 \times 10^{-6}$ | 91 | Glass | 0.05 | |
| 8 | .5 | $BF_3$ | $7.0 \times 10^{-4}$ | 28[b] | ..... | ... | |
| 8 | .5 | $B(OCH_3)_3$ | $5.0 \times 10^{-4}$ | 16[b] | ..... | ... | |
| Runs with diazoethane | | | | | | | |
| 8.5 | .61 | $CuSO_4$ | Insol.[c] | 59 | Glass | ... | |
| 8.5 | .61 | Cupric stearate | $6.2 \times 10^{-6}$ | 95 | Glass | 0.12 | |
| 8.5 | .61 | $B(n\text{-}OC_4H_9)_3$ | $2.0 \times 10^{-4}$ | 23[b] | ..... | ... | |
| 8.5 | .61 | $BF_3$ | $5.0 \times 10^{-4}$ | 25[b] | ..... | ... | |
| Runs with diazomethane | | | | | | | |
| 0 | 0.55 | $BF_3$ | $5.0 \times 10^{-4}$ | 100 | Wax | 16.2[d] | |
| 0 | .55 | Cupric stearate | $12.8 \times 10^{-6}$ | 9[b] | ..... | ... | |
| 0 | .55 | $B(OCH_3)_3$ | $2.0 \times 10^{-4}$ | 15[b] | ..... | ... | |
| Runs with diazomethane–diazoethane mixtures[e] | | | | | | | |
| 0 | 0.51(5/1) | $B(OCH_3)_3$ | $2.0 \times 10^{-4}$ | 80 | Rubber | 7.3 | |
| 0 | .41(8/1) | $BF_3$ | $0.5 \times 10^{-3}$ | 94 | Rubber | 8.7 | |
| 0 | .49(5/1) | $BF_3$ | $0.8 \times 10^{-3}$ | 90 | Rubber | 7.2 | |
| 0 | .22(4/1) | $BF_3$ | $0.5 \times 10^{-3}$ | 91 | Rubber | 6.19 | $2.0 \times 10^6$ |
| 0 | .56(4/1) | $BF_3$ | $5.0 \times 10^{-3}$ | 98 | Rubber | 6.3 | $2.07 \times 10^6$ |
| 0 | .55(1/1) | $BF_3$ | $0.5 \times 10^{-3}$ | 40 | Rubber | 2.2 | |
| 0 | .53(4/1) | Cupric stearate | $12.8 \times 10^{-6}$ | 8 | ..... | ... | |

[a] Conversions are based upon the amount of methanol-insoluble polymer obtained after total decomposition of diazohydrocarbon. [b] Reaction exhibited a pronounced decrease in rate between 10 and 25% decomposition and proceeded at nearly the uncatalyzed rate for the remainder of the reaction. Successive additions of catalyst produced only a temporary acceleration of decomposition rate. [c] 0.3 g. of $CuSO_4$ suspended with stirring in 30 ml. of solution. [d] Determined in xylene at 120°. [e] The numbers in parentheses under column 2 refer to the mole ratio of diazomethane to diazoethane.

stearate also have been found to be first order in catalyst concentration.

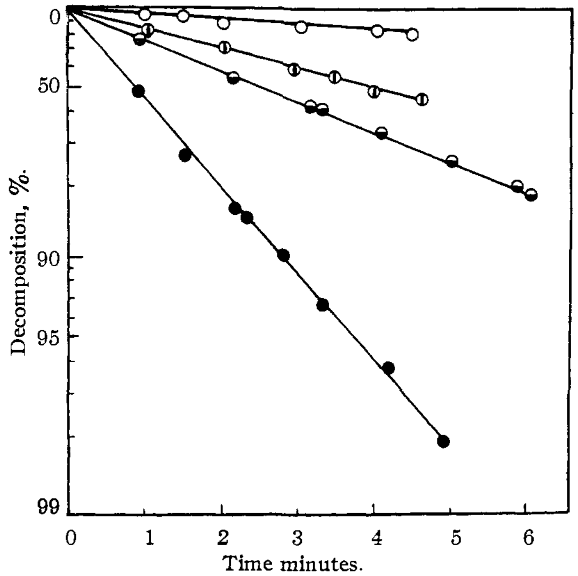

Fig. 2.—Decomposition of a 4:1 molar mixture of diazomethane–diazoethane in ether at 0° catalyzed by boron trifluoride; dependence of rate on catalyst concentration: ○, $BF_3 = 7.05 \times 10^{-4}$; ◐, $BF_3 = 17.6 \times 10^{-4}$; ⊖, $BF_3 = 35.2 \times 10^{-4}$; ●, $BF_3 = 70.0 \times 10^{-4}$; diazomethane = 0.224 *M*, diazoethane = 0.056 *M*.

**Dependence of Decomposition Rate on Temperature.**—The rates of decomposition of a number of diazohydrocarbons of 0.3 *M* concentration in ether at 22° catalyzed by $12 \times 10^{-6}$ *M* cupric stearate were observed to decrease in the order diazoethane > diazobutane > diazohexane > diazoöctane > diazodecane > phenyldiazomethane. In the case of diazobutane and diazoethane, the rates of decomposition in ether catalyzed by cupric stearate were measured at four temperatures in the range 3–22°. The over-all activation energy for the decomposition of diazobutane was calculated to be 20.6 ± 0.9 kcal./mole and for the decomposition of diazoethane, 8.5 ± 0.4 kcal./mole. The increased activation energy for the decomposition of the higher homolog apparently coincides with the relative stabilities of the two diazohydrocarbons at room temperature.

**Dependence of Molecular Weight on Concentration of Reactants.**—Table I summarizes the results of several runs on the decomposition of diazobutane, diazoethane, diazomethane and mixtures of the latter two diazohydrocarbons under the influence of various catalysts. A considerably greater number of runs were made than have been presented in Table I. However, it is the intention in constructing the table to include only those runs which resulted in the highest values for conversion (column 5) and limiting viscosity number of polymer (column 7) obtained with a given catalyst and diazohydrocarbon system. Weight average molecular weights, $\bar{M}_w$, are listed in the last column for two polymers derived from a 4:1 molar mixture of diazomethane–diazoethane.

It is interesting to note that cupric stearate effectively catalyzes the decomposition of diazohydrocarbons above diazomethane and is a relatively poor catalyst for diazomethane decomposition while boron trifluoride effectively catalyzes the decomposition of diazomethane and its mixtures with diazoethane.

Since the polymers derived from diazobutane and diazoethane are of low viscosity, it was not possible to estimate the effect of catalyst and diazohydrocarbon concentrations on molecular weight. On the other hand, the polymers derived from diazomethane–diazoethane mixtures are of high molecular weight and, in contrast with the polymer obtained from diazomethane, soluble in toluene at room temperature. Accordingly a number of polymer samples in addition to those reported in Table I were prepared for molecular weight evaluation from a 4:1 molar ratio of diazomethane–diazoethane using boron trifluoride catalyst. The initial concentration of the diazohydrocarbon mixture was varied over a tenfold range and the concentration of boron trifluoride over a fifteen-fold range. It is seen from the viscosity values presented in Table II that there is no significant variation in the molecular weight of the polymer samples with the concentration of reactants. Since the decomposition reactions were heterogeneous due to the insolubility of the polymer in ether, the zero-order dependence of molecular weight on concentration of reactants might be attributed to a diffusion controlled condition of diazohydrocarbon to precipitated chain ends. On the other hand, the rates of decomposition of the same diazohydrocarbon mixture in ether catalyzed by boron trifluoride have been observed to follow a first-order dependence on diazohydrocarbon and catalyst concentrations which is not consistent with the hypothesis of a diffusion controlled process.

TABLE II

DECOMPOSITION OF A 4:1 MOLAR MIXTURE OF DIAZOMETHANE–DIAZOETHANE IN ETHER AT 0° CATALYZED BY BORON TRIFLUORIDE

Effect of Catalyst and Diazohydrocarbon Concentrations on Molecular Weight of Polymer

| Total $RCHN_2$ concn., moles/l. | Catalyst, moles/l. × $10^4$ | Conversion, % | $[\eta]^{20°}$ toluene, dcl./g. |
|---|---|---|---|
| 0.0548 | 5.0 | 62 | 7.48 |
| .223 | 5.0 | 91 | 6.19 |
| .335 | 5.0 | 89 | 5.3 |
| .446 | 5.0 | 93 | 5.5 |
| .558 | 5.0 | 99 | 6.3 |
| .558 | 2.5 | 83 | 6.1 |
| .558 | 10.0 | 92 | 5.9 |
| .558 | 14.0 | 97 | 7.46 |
| .558 | 24.0 | 92 | 6.9 |
| .558 | 30.0 | 90 | 7.3 |
| .558 | 50.0 | 98 | 6.3 |

**Decomposition of Other Diazohydrocarbons.**—Attempts to prepare polymeric derivatives from diazohexane, phenyldiazomethane, diazoöctane and diazodecane were unsuccessful. Diazohexane, for example, decomposed readily but more slowly than diazobutane in the presence of cupric stearate to yield a liquid product tentatively identified from its freezing point of −32.6° to be the dimer 6-dodecene. It should be noted, however, that while our studies have indicated that the decomposition of diazohydrocarbons above diazobutane does not produce polymeric derivatives, mixtures of the higher diazohydrocarbons with diazomethane have been reported[5e] to produce high molecular weight copolymers. The evidence for the formation of a real copolymer rather than a mixture of polymers is based upon the appearance of new fundamental bands in the infrared spectrum of the copolymer which are not found in the individual polymers[5e] and also by comparison of the solubilities of the individual polymers and the copolymers.

**Inhibition of Decomposition.**—Qualitative observations concerning the inhibitory effect of several organic compounds on the decomposition of diazoethane catalyzed by cupric stearate and the decomposition of a 4:1 molar mixture of diazomethane–diazoethane catalyzed by boron trifluoride in ether are as follows. The free radical inhibitors hydroquinone, *t*-butylcatechol and α,α-diphenyl-β-picrylhydrazyl in molar amounts up to 10-fold greater than the catalyst employed imparted no significant inhibition of decomposition of diazohydrocarbon nor was the percentage conversion to polymer altered. On the other hand, the introduction of primary, secondary or tertiary amines including *n*-butylamine, diethylamine and triethylamine in molar amounts equivalent to the quantity of catalyst employed effected total inhibition of the decomposition reaction. These observations strongly indicate that the decomposition is not a radical reaction. Kantor and Osthoff[6] have concluded that the decomposition of diazomethane catalyzed by boron trifluoride is an ionic mechanism.

## Discussion

**Decomposition Initiated by Boron Trifluoride.**—A reaction mechanism consistent with the observed kinetics is the following. Let the diazohydrocarbon in its two main mesomeric forms[12] be represented by I and II where R is H or $CH_3$; and

$$\underset{\text{I}}{:\overset{(-)}{C}HR\text{—}\overset{(+)}{N}\equiv N:} \longleftrightarrow \underset{\text{II}}{CHR = \overset{(+)}{N} = \underset{\cdot\cdot}{\overset{(-)}{N}}:}$$

the catalyst, boron trifluoride, complexed with a cocatalyst[13] HX such as water, methyl alcohol[14] or possibly ether[15] be represented by $[BF_3X]^-[H]^+$. Initiation ($k_i$):

$$[BF_3X]^-[H]^+ + :\overset{(-)}{C}HR\text{—}\overset{(+)}{N}\equiv N \longrightarrow \underset{\text{III}}{[CH_2R\text{—}N\equiv N]^+[BF_3X]^-} \quad (1)$$

Propagation ($k_p$):

$$[CH_2R\equiv N\text{—}N]^+[BF_3X]^- + n:\overset{(-)}{C}HR\text{—}\overset{(+)}{N}\equiv N \longrightarrow\longrightarrow\longrightarrow$$

$$RCH_2(CHR)_{n-1}[CHR\text{—}N\equiv N]^+[BF_3X]^- + nN_2 \quad (2)$$

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(12) B. L. Crawford, W. H. Fletcher and D. A. Ramsay, *J. Chem. Phys.*, **19**, 406 (1951).

(13) Proceedings of Conference at University of North Staffordshire on "Cationic Polymerization and Related Complexes," P. H. Plesch, editor, W. Heffer and Sons, Cambridge, 1953, p. 145; P. H. Plesch, *J. Polymer Sci.*, **12**, 481 (1954).

(14) Methyl alcohol may be formed in the system by reaction of diazomethane with water.

(15) A. G. Evans, *J. Appl. Chem.*, **1**, 240 (1950).

**Termination by Transfer** ($k_t$):

$$\mathrm{RCH_2(CHR)_{\mathit{n}-1}[CHR{-}N{\equiv}N]^+[BF_3X]^- + I \longrightarrow}$$
$$\mathrm{RCH_2(CHR)_{\mathit{n}-2}CR{=}CHR\ +}$$
$$\mathrm{[CH_2R{-}N{\equiv}N]^+[BF_3X]^- + N_2} \quad (3A)$$

or

$$\mathrm{RCH_2(CHR)_{\mathit{n}-1}[CHR{-}N{\equiv}N]^+[BF_3X]^- + II \longrightarrow}$$
$$\mathrm{RCH_2(CHR)_{\mathit{n}-1}CR{=}N{-}N{=}CHR + [BF_3X]^-[H]^+ + N_2} \quad (3B)$$

By assuming a steady state condition for the ion pair, III, the rate of decomposition of diazohydrocarbon is given by equation 4.

$$\text{Rate} = (k_i k_p/k_t)[\mathrm{M}][\mathrm{Cat}] \qquad (4)$$

where [M] is the concentration of diazohydrocarbon, [Cat] the concentration of the boron trifluoride cocatalyst system and $k_i$, $k_p$ and $k_t$ the specific rate constants for the initiation, propagation and termination steps, respectively. The number average degree of polymerization of polymer, $\bar{P}_n$, is defined by the expression

$$\bar{P}_n = (k_p/k_t) \qquad (5)$$

Equations 4 and 5 are in agreement with the observed kinetic results wherein the decomposition rate is first order with respect to the concentrations of catalyst and diazohydrocarbon while the molecular weight of polymer is independent of the concentration of reactants.

The initiation step in the above mechanism is postulated to involve the reaction of a boron trifluoride cocatalyst complex with diazohydrocarbon. The resultant ion pair III is analogous to the unstable, alkyl diazonium ions such as $CH_3N_2^+$-$Cl^-$. The formation of alkyl diazonium ion intermediates also has been postulated in the acid-catalyzed decomposition of diazobutene and diazopentane.[16] The nature of the boron trifluoride–cocatalyst complex cannot be ascertained from the present investigation nor has its existence been proved. The reason for postulating its existence is solely based upon the experience of other investigators of ionic polymerizations.[13]

The propagation step, equation 2, is postulated to involve the reaction of diazomethane or diazoethane with a diazonium cation followed by the loss of nitrogen and the formation of a new diazonium cation. It is also likely that the unstable diazonium ion rapidly eliminates a nitrogen molecule in which case propagation proceeds *via* the attack of a carbonium ion on the diazohydrocarbon

$$\mathrm{\sim\!\!-\overset{+}{C}HR[BF_3X]^- + :\overset{(-)}{C}HR{-}\overset{(+)}{N}{\equiv}N \longrightarrow}$$
$$\mathrm{\sim CHR[CHRN{\equiv}N]^+[BF_3X]^- \longrightarrow}$$
$$\mathrm{\sim CHR\overset{+}{C}H_2[BF_3X]^- + N_2} \quad (6)$$

Termination of growing chains by either step 3A or 3B leads to polymer containing terminal unsaturation and in addition, by step 3B, a polymer containing two nitrogen atoms per polymer molecule. Unfortunately, due to the high molecular weights of the polymer (column 8, Table I), it is not possible to specify the nature of the polymer and groups by conventional techniques. It is known,[5e] however, that the higher series of diazohydrocarbons produce decomposition products that correspond to the dimeric structures obtained in termination by steps 3A or 3B. It is interesting to note that the addition of increasing amounts of diazoethane to diazomethane apparently results in the formation of a lower molecular weight polymer as evidenced by the decreasing viscosity values of the polymers reported in Table I. On the basis of the proposed mechanism this effect can only be due to a decrease in the propagation rate, or an increase in the termination rate with increasing mole ratios of diazoethane to diazomethane.

**Decomposition Initiated by Cupric Stearate.**—There is little or no evidence available from the present work concerning the nature of the initiation step in the decomposition reaction catalyzed by cupric stearate. Experiments with inhibitors have indicated that the reaction is not of a free radical nature since radical inhibitors such as $\alpha,\alpha$-diphenyl-$\beta$-picrylhydrazyl and *t*-butylcatechol had no effect on the reaction. Whereas the postulated existence of a cocatalyst complex conveniently describes the initiation step with boron trifluoride catalysis, it is difficult to picture a related complex with cupric stearate. All that might be conjectured is that the cupric ion complexes with the diazohydrocarbon and/or the ether solvent to form an active species that propagates the decomposition reaction.

Brooklyn, N. Y.

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(16) D. V. Curtin and S. M. Gerber, This Journal, **74**, 4052 (1952).