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The Mechanism of Decomposition of Azo Compounds. III. Cage Effects with Positively Charged Geminate Radical Pairs

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Thermal decomposition of two azobisamidines and their conjugate acids has been studied. In each case the rate of decomposition of the first conjugate acid is considerably faster than that of the free base. Little or no further increase is observed when the rates of decomposition of the second conjugate acids are measured. The efficiencies of radical production from the doubly charged, second conjugate acids are only slightly higher than from the neutral azoamidines. We conclude that electrostatic effects on the extent of geminate recombination are small.

Careful studies of the decomposition of azobisisobutyronitrile (ABN)²⁻⁴ and 1,1'-azocyanocyclohexane⁵ have shown that the rates of production of scavengeable radicals from these initiators are less than twice the rates of decomposition. The discrepancy is attributed to coupling and disproportionation of geminate radical pairs, formed by the primary decomposition process, before the pair has been separated by diffusion. This effect, which was first described by Franck and Rabinowitch,⁶ has been called the "cage" effect since the time of encounter is prolonged, relative to the gas phase, because the geminate pair is surrounded by a "cage" of solvent molecules.

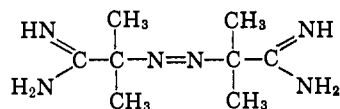
The simple model for the "cage" effect treats all molecules as hard spheres^{7,8} and takes no account of the effects of positive or negative interaction potentials between the radicals on the competition between coupling and separation by diffusion. Such factors are difficult to include in the theoretical treatment in more than a formal sense so an experimental approach to their evaluation is indicated. A particularly interesting case is that in which pairs of electrically charged radicals are generated. Comparison of the extent of geminate recombination in such a case with that observed with similarly constituted, neutral radicals should provide preliminary orientation as to the effect of electrostatic repulsion on geminate recombination. The need for such orientation is illustrated by the fact that this question has arisen in connection with discussions of the various possible mechanisms of the benzidine rearrangement. Since kinetic studies show that the rearrangement is usually a two-proton process, the observed intramolecularity of the reaction would require extensive geminate coupling of pairs of cation radicals if the reaction does involve a radical mechanism. At least one author⁹ has rejected the mechanism completely on the basis of the expectation that electrostatic repulsion should reduce geminate coupling to a negligible level.

Comparison of the efficiencies of radical production from azobisamidines and their second conjugate acids seemed to provide a reasonable means for preliminary evaluation of electrostatic effects on geminate recombination. As has been recently reported,¹⁰ the dihydrochloride of azobisisobutyramidine undergoes decomposition at a convenient rate and initiates the polymerization of vinyl monomers. We wish to report a study of

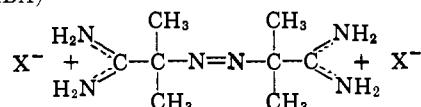
the efficiency of radical production from this compound, the neutral amidine and a related acid-base pair.

Results and Discussion

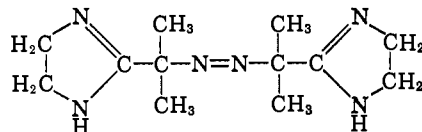
The compounds studied were azobisisobutyramidine (ABA, I) two derived salts IIa and IIb, azobis-N,N'-dimethyleneisobutyramidine, (ADMBA, III) and the derived dinitrate IV. Decomposition of the first conjugate acids was also studied although the mono-salts were not isolated.



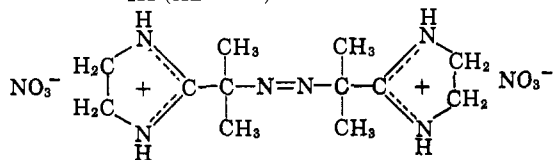
I (ABA)



IIa, X = Cl⁻(ABA·2HCl)
IIb, X = NO₃⁻(ABA·2HNO₃)

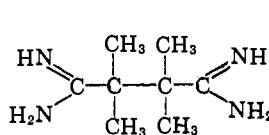


III (ADMBA)

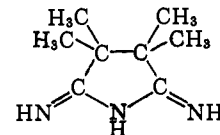


IV (ADMBA·2HNO₃)

Choice of a solvent for the study was not a trivial problem. Amidinium ions are so weakly acidic that they cannot be stoichiometrically neutralized in aqueous solutions. Furthermore, hydrolysis becomes rather rapid in solutions in which the pH is above 12. On the other hand, bisamidinium salts are sparingly soluble in most organic solvents. Fortunately the dinitrates of both ABA and ADMBA proved to be soluble in dimethyl sulfoxide (DMSO) which is also an adequate solvent for the free bases. Although decomposition products have been studied, a material balance has not been obtained in any reaction. Dougherty¹⁰ reported the isolation of a series of products from the decomposition of ABA·2HCl in water. All products isolated may be considered to be derived from hydrolysis of tetramethylsuccinamide (V) or tetramethylsuccinimide (VI).



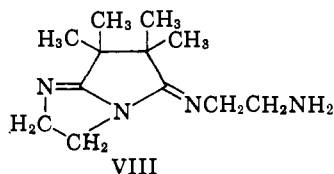
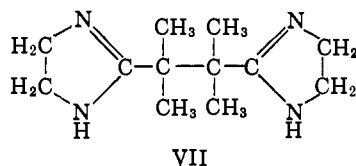
V



VI

- (1) National Institutes of Health Predoctoral Fellow, 1960-1962.
- (2) G. S. Hammond, J. N. Sen and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).
- (3) G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin and R. T. Keys, *ibid.*, **82**, 5394 (1960).
- (4) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).
- (5) C.-H. S. Wu, G. S. Hammond and J. Wright, *ibid.*, **82**, 5386 (1960).
- (6) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).
- (7) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955).
- (8) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).
- (9) M. J. S. Dewar, "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths, London, 1959, p. 197.
- (10) T. J. Dougherty, *J. Am. Chem. Soc.*, **83**, 4849 (1961).

The nitrate of VI was isolated in 35% yield from the decomposition of $\text{ABA} \cdot 2\text{HNO}_3$ in DMSO. Similarly, a 28% yield of the nitrate of bisamidine VII was isolated from the products of decomposition of $\text{ADMBA} \cdot 2\text{HNO}_3$ in DMSO. The mother liquor from which the salt was isolated was subjected to hydrolysis and an ether extract of the oily product was subjected to gas chromatography. The chromatogram indicated the presence of several compounds, one of which was tentatively identified as isobutyric acid by comparison of retention times. Decomposition of ADMBA in DMSO gave a new compound which was apparently isomeric with VII. The compound gave a rather complicated n.m.r. spectrum in chloroform solution, showing multiple resonance signals in both the methyl and methylene regions of the spectrum. However, in 15% sulfuric acid solution the compound shows the very simple spectrum expected of VII. A sample dissolved in dilute aqueous acid initially showed a spectrum very similar to that of chloroform solutions, but slowly changed to the simpler spectrum shown immediately by solutions in more concentrated acid. We conclude that the product isolated by concentration of the DMSO solution is an unsymmetrical isomer of VII, such as VIII



No attempt was made to isolate products from decomposition of neutral ABA; however, it was determined that a large amount of ammonia was produced, indicating that coupling to form V, followed by cyclization to VI, occurred. Isolated yields of pure products were not high in any case but infrared spectra of mother liquors indicated the presence of considerable additional amounts of the same, or similar, products. The results suggest that decomposition gives amidinoalkyl radicals which react principally by carbon-carbon coupling with some disproportionation. The results are similar to those which have been observed in the decomposition of azonitriles^{2,11} and azoesters.¹²

Since little is known about the reactivity of DMSO toward free radicals it was conceivable that the solvent might react as a radical scavenger. This possibility was rendered improbable by the observation that decomposition of ABN in DMSO gives an 89% yield of tetramethylsuccinonitrile.

Decomposition Rates.—Rates of decomposition of the azo compounds were measured by monitoring the evolution of nitrogen. The results are summarized in Table I.

The values for the rates of decomposition of AAB salts in water are very similar to those measured by Dougherty¹⁰ for $\text{ABA} \cdot 2\text{HCl}$ using a spectrophotometric method. It is also noteworthy that solvent effects on the decomposition rates are almost negligibly small. Activation parameters calculated for $\text{ADMBA} \cdot 2\text{HNO}_3$ in DMSO are: $\Delta H^\ddagger = 26$ kcal. mole⁻¹ and $\Delta S^\ddagger = +1$ e.u.; those for ADMBA in DMSO-cumene

(11) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

(12) A. F. Bickel and W. A. Waters, *ibid.*, **69**, 312 (1950).

TABLE I
FIRST-ORDER RATE CONSTANTS FOR DECOMPOSITION OF AZO-AMIDINES

| Azo compound | T, °C. | Solvent | k × 10 ⁵ , sec. ⁻¹ |
|------------------------------------|--------|----------------------------|--|
| $\text{ABA} \cdot 2\text{HCl}$ | 70 | Water | 15.2 ± 0.3 |
| $\text{ABA} \cdot 2\text{HNO}_3$ | 60 | DMSO-cumene ^a | 4.86 |
| $\text{ABA} \cdot 2\text{HNO}_3$ | 70 | DMSO-cumene ^a | 15.3 |
| $\text{ABA} \cdot 2\text{HNO}_3$ | 70 | DMSO | 17.6 |
| ABA | 70 | DMSO | 0.368 ± 0.003 ^b |
| $\text{ADMBA} \cdot 2\text{HNO}_3$ | 60 | DMSO | 20.6 ± 0.4 |
| $\text{ADMBA} \cdot 2\text{HNO}_3$ | 60 | DMSO-tetralin ^a | 21.3 |
| $\text{ADMBA} \cdot 2\text{HNO}_3$ | 60 | DMSO-cumene ^a | 20.0 ± 0.9 |
| $\text{ADMBA} \cdot 2\text{HNO}_3$ | 70 | DMSO | 66.4 ± 0.4 |
| $\text{ADMBA} \cdot 2\text{HNO}_3$ | 70 | DMSO-cumene | 69.7 ± 1.2 |
| $\text{ADMBA} \cdot 2\text{HNO}_3$ | 75 | DMSO | 108 |
| ADMBA | 60 | DMSO-tetralin ^a | 1.09 |
| ADMBA | 75 | DMSO-cumene ^a | 8.04 ± 0.14 |
| ADMBA | 80 | DMSO | 17.9 |
| ADMBA | 80 | DMSO-cumene ^a | 13.9 ± 0.1 |
| ADMBA | 85 | DMSO-cumene ^a | 26 ± 1 |

^a Two volumes DMSO to one volume of co-solvent. ^b Total rate of gas evolution, nitrogen plus ammonia.

are: $\Delta H^\ddagger = 29$ kcal. mole⁻¹ and $\Delta S^\ddagger = +7$ e.u. Since the data are limited and the temperature ranges small, these values must be considered approximate.

Measurement of the rate of decomposition of ABA was fraught with difficulty because ammonia was evolved along with nitrogen. The decomposition rates were very slow at temperatures of interest for the principal purpose of this study. Consequently it was not practical to measure the value of V_∞ accurately. Several attempts were made to estimate the rate of nitrogen evolution by inclusion of acidic scavengers in the vapor space. The rates of gas evolution were decreased substantially, but the results were not quantitatively consistent. In one run the rate of ammonia production was measured by passing a stream of nitrogen through the reaction mixture and into standard aqueous acid. The pH of the solution was monitored with a pH meter and additional aliquots of standard acid were added whenever the pH rose to 7. During the early part of the run the data were erratic and small details of experimental procedure were continuously revised. Good data were collected between the 100th and 190th hours; the experiment was then terminated. The reaction mixture was maintained at 70° throughout the experiment. The rate of ammonia evolution decreased during the period when good data were obtained. An attempt was made to fit the data to eq. 1 and 2. The value obtained for χ was 1.35.

$$-d[\text{ABA}]/dt = k_0[\text{ABA}] \quad (1)$$

$$d[\text{NH}_3]/dt = \chi k_0[\text{ABA}] \quad (2)$$

This is physically unrealistic if it is assumed that cyclization is very fast in comparison with decomposition, since χ should be 1.0 or less. The result almost certainly indicates that the loss of ammonia by the cyclization reaction is not fast enough to allow tetramethylsuccinamidine to be treated by the steady state approximation, *i.e.*, a significant amount of amidine must have been accumulated in solution during the first hundred hours of the reaction. Since it appeared that only a very tedious study would allow accurate dissection of the rate of gas evolution from ABA the project was abandoned in favor of a quantitative study of ADMBA which evolves no gas other than nitrogen on decomposition.

The fact that the decomposition of $\text{ABA} \cdot 2\text{HNO}_3$ and $\text{ADMBA} \cdot 2\text{HNO}_3$ is much faster than the rates of decomposition of the neutral amidines is intriguing. The acceleration might be attributed either to stabilization

of the radicals by protonation or to relief of electrostatic repulsion, in the second conjugate acids, by the decomposition reaction. The question was resolved by studying the rates of decomposition of the first conjugate acids. Slightly different methods were used for investigation of ABAH^+ and ADMBAH^+ . In the former case, measured amounts of concentrated hydrochloric acid were added to DMSO solutions of ABA. The rates were estimated by measurement of the initial rates of nitrogen evolution. The results, which are summarized in Table II, are expressed in terms of pseudo-first-order rate constants according to eq. 3.

$$d \text{ gas}/dt = kT_B \quad (3)$$

$$T_B = [\text{ABA}] + [\text{ABAH}^+] + [\text{ABAH}_2^{++}]$$

Since amidines are much stronger bases than ammonia, we presume that comparable fractions of the gas were ammonia in all of the runs reported in Table II.¹³

TABLE II

INITIAL RATES OF GAS EVOLUTION FROM ABA WITH ADDED HYDROCHLORIC ACID IN DMSO AT 70°

| T_{ABA} , moles/l. $\times 10^4$ | $[\text{HCl}]$, moles/l. $\times 10^3$ | $k \times 10^4$, sec. ⁻¹ |
|--|--|--------------------------------------|
| Any | 0 | 3.68 ^a |
| 2.526 | 1.12 | 15.62 |
| 2.506 | 4.33 | 21.88 |
| 2.521 | 6.25 | 30.12 |

^a From Table I.

The variation of the rate of decomposition of ADMBA with varying acid concentration was investigated by studying the rates of nitrogen evolution from solutions from weighed amounts of ADMBA and $\text{ADMBA} \cdot 2\text{HNO}_3$. Data for gas evolution were plotted against time and tangents to the curves were determined at times after initial irregularities¹⁴ had subsided. The values of pseudo-first-order rate constants were calculated by use of eq. 4

$$dN_2/dt = k(T_B)_0 e^{-kt} \quad (4)$$

The values of k are summarized in Table III.

TABLE III

INITIAL RATES OF NITROGEN EVOLUTION FROM MIXTURES OF ADMBA AND $\text{ADMBA} \cdot 2\text{HNO}_3$ IN DMSO AT 60°

| ADMBA, ^a mole $\times 10^4$ | $\text{ADMBA} \cdot 2\text{HNO}_3$, ^a moles $\times 10^4$ | $k \times 10^4$, sec. ⁻¹ |
|---|--|--------------------------------------|
| 0.471 | 1.355 | 1.98 |
| .256 | 1.331 | 2.11 |
| .824 | 1.051 | 2.03 |
| .745 | 0.810 | 1.84 |
| .809 | 0.399 | 1.29 |
| None | 1.198 | 2.06 |
| 0.655 | None | 0.101 |

^a Amount of material dissolved in 5 ml. of DMSO.

The values of the pseudo-first-order rate constants should be given by eq. 5.

$$kT_B = k_0[\text{B}] + k_1[\text{BH}^+] + k_2[\text{BH}_2^{++}] \quad (5)$$

The values of k_0 and k_2 are known. Therefore, the value of k_1 can be calculated if the concentrations of the three species B, BH^+ and BH_2^{++} are known or assumed.¹³ Since the amidines are very strong bases, virtually all of the acid in the system will exist as either BH^+ or BH_2^{++} . The relative amounts of the three

(13) The relative amounts of NH_3 and N_2 in the gas from the ABA systems are not known; however, $(\text{NH}_3)/(\text{N}_2) < 1$ by the stoichiometry of the reaction. In order to calculate k_1 from eq. 5, each k in Table II is divided by 2. This gives the maximum correction and will make values of k_1 minimum values.

(14) The rate of gas evolution was slow and irregular during the first few minutes of all runs. This effect is attributed to changes in the rate of reaction and the vapor pressure of the solvent during the warm-up period.

amidines will be determined by the ratio of the basicity constants K_1 and K_2 . Semiquantitative examination of the data shows that the values of k_1 , for both systems, must be larger than values of k_0 . The data in Table II show that addition of a small amount of acid produces a large increase in the decomposition rate. The only alternative would be to assume that the second basicity constant K_2 is much larger than K_1 , a most unlikely possibility. The data in Table III are even more convincing. The value of the pseudo-first-order rate constant does not decrease measurably when substantial amounts of B are added to BH_2^{++} . This is only possible if most of the B is converted to BH^+ with the rate of decomposition of the latter being virtually the same as the rate of decomposition of BH_2^{++} . In order to interpret the data, it is also necessary to assume that no significant change occurs in the distribution of the total azoamidine among the three species during the early part of an experiment (15–20% conversion). This assumption is imminently reasonable because the products probably are comparable to the reactants in basicity. Subject to the assumptions stated, we may calculate the values of k_1 as a function of assumed values of K_1/K_2 . The results are summarized in Table IV. The calculated values are very nearly the same if the ratio is assumed infinite as they are if the ratio is assumed to be four, the value expected on a statistical basis if the inherent basicity of all amidine groups is assumed to be the same.

TABLE IV

RATE CONSTANTS FOR DECOMPOSITION OF AZOAMIDINES AND AZOAMIDINIUM IONS

| Species | T , °C. | Assumed value of K_1/K_2 | $k \times 10^4$, sec. ⁻¹ |
|-----------------------------------|-----------|----------------------------------|---|
| ADMBA | 60 | .. | 1 ^a |
| ADMBAH ⁺ | 60 | 4 | 25 ± 3 ^b |
| ADMBAH ⁺ | 60 | ∞ | 20 ± 1 ^b |
| ADMBAH ₂ ⁺⁺ | 60 | .. | 20.6 ± 0.4 ^a |
| ABA | 70 | .. | 0.2 ^a |
| ABAH ⁺ | 70 | 4 | 6 ± 1 ^b |
| ABAH ⁺ | 70 | ∞ | 6 ± 1 ^b |
| ABAH ₂ ⁺⁺ | 70 | .. | 17 ^a |

^a Measured; see Tables I and II. ^b Calculated from data in Tables II and III.

The results lead immediately to the conclusion that relief of electrostatic repulsion is not a significant accelerating factor in the decomposition of the second conjugate acids. Of course, this does not mean that no electrostatic repulsion exists; the transition state for decomposition may be expanded relatively little compared to the ground state of the ion.

A second point of interest arises. Common opinion holds that the decomposition of azo compounds involves complex fragmentation with simultaneous breaking of both C–N bonds. The best evidence in support of this view comes from consideration of the rates of decomposition of symmetrical and unsymmetrical azoalkanes.¹⁵ The rate of decomposition of propane-2-azomethane is approximately the geometric mean of the rates of decomposition of the two symmetrical compounds. Substituent effects on the rates of decomposition of 1-azobis-1-phenylethanes¹⁶ give the same implication. The results imply that the rate of fragmentation of $\text{R}-\text{N}=\text{N}-\text{R}'$ is sensitive to factors influencing the stability of both R and R'; that is, the driving force due to radical stabilization is cumulative. Application of the same argument to the data reported

(15) H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927); **50**, 714 (1928); **51**, 2134 (1929).

(16) S. G. Cohen, S. J. Groszoz and D. B. Sparrow, *ibid.*, **72**, 3947 (1950).

TABLE V
 EFFICIENCY OF RADICAL PRODUCTION FROM AZO COMPOUNDS IN DMSO-HYDROCARBON MIXTURES

| Initiator | T, °C. | Solvent ^a | [Inhibitor] ₀ , moles × 10 ^{4b} | [RN ₂ R] ₀ , moles × 10 ^{4b} | t ₁ , min. | a |
|-------------------------|--------|----------------------|--|--|-----------------------|--------------|
| ABN | 70 | DMSO-cumene | 1.78 | 4.02 | 27.4 | 0.573 |
| ABN | 70 | DMSO-cumene | 2.09 | 3.05 | 42.9 | .578 |
| ABN | 70 | DMSO-cumene | 2.09 | 3.05 | 43.1 | .576 |
| ABA·2HNO ₃ | 70 | DMSO-cumene | 1.01 | 0.250 | 119.3 | .609 |
| ABA·2HNO ₃ | 70 | DMSO-cumene | 0.544 | .261 | 46.5 ± 0.8 | .60 ± 0.008 |
| ABA·2HNO ₃ | 70 | DMSO-cumene | .522 | .261 | 44.4 ± 0.1 | .598 ± 0.008 |
| ADMBA·2HNO ₃ | 60 | DMSO-tetralin | .582 | .210 | 44.7 | .66 |

^a Solvent prepared with two volumes DMSO and one volume of hydrocarbon. ^b Amount dissolved in 25.0 ml. of solvent.

here would lead to the conclusion that decomposition of azoamidines is stepwise. The activation entropies for decomposition of ADMBA and ADMBA·2HNO₃ are +7 and +1 e.u., respectively. These values fall within a range which appears "normal" for azo compounds, e.g., azobisdiphenylmethane, +2 e.u.,¹⁷ ABN, +3 e.u.,¹⁸ and azobis-1,1'-phenylethane, +7.¹⁶ Consequently the criterion suggested by Bartlett¹⁹ for detection of concerted fragmentation reactions does not point to any mechanistic discontinuity in the decomposition of azo compounds. Neither criterion can be considered as rigorous for establishment of mechanism so we merely suggest that the timing of decomposition of azo compounds be retained as an open question.

Efficiency of Radical Production.—There are two general procedures for measurement of rates of radical production in solution, measurement of the rate of disappearance of a highly reactive scavenger and measurement of the rate of a radical chain reaction initiated by the radical source. The latter procedure does not yield absolute values for rates of radical generation unless the rates of other steps in the chain process are known independently; however, comparison of data obtained with two initiators gives their relative efficiencies directly if their individual decomposition rates are known. Data from any measurement must, however, be carefully scrutinized. Powerful scavengers may undergo unwanted side reactions with the initiators, or the stoichiometry of scavenging reactions may be uncertain. The rates of chain reactions may be affected by inefficient utilization of primary radicals for reasons other than geminate recombination, or by reaction of chain-carrying radicals with the initiator. Such complications have been encountered in this study, but we feel that by suitable choice of experiments we have been able to arrive at reliable values for the efficiencies of ABAH₂⁺⁺, ADMBA and ADMBAH₂⁺⁺. A tentative value for the efficiency of ABA has also been obtained but is less certain because of the above-mentioned complication, due to evolution of ammonia, in estimation of the rate of decomposition. We have not attempted to measure the efficiency of radical production from the first conjugate acids.

Rates of Radical Production from Second Conjugate Acids.—Scavenging by iodine is obviously not feasible because iodine reacts rapidly with amidines.¹⁰ Therefore, we turned to scavenging by oxidation inhibitors. The method, which has been described in detail elsewhere,² involves measurement of the inhibition periods produced by known amounts of anti-oxidants. Unless the radicals from the initiator are exceptionally unreactive toward oxygen, the method has the advantage that the radical being scavenged is always RO₂, usually derived from an oxidizable hydrocarbon in the reaction mixture. Consequently, stoichiometric relationships established with one initiator

are likely to be applicable to another. The inhibitor used in this study was 2,6-di-*tert*-butyl-*p*-cresol which is known to stop two oxidation chains per molecule. The inhibition periods for oxidation in DMSO initiated by ABAH₂⁺⁺ and ADMBAH₂⁺⁺ were well defined. The efficiency factors were calculated from eq. 6.

$$a = \frac{[\text{inhibitor}]_0}{[\text{RN}_2\text{R}]_0(1 - e^{-kt_1})} \quad (6)$$

where k = rate constant for decomposition of RN₂R and t_1 = duration of the inhibition period.

For purposes of comparison the efficiency of initiation by ABN was also determined in the same reaction medium. All data are summarized in Table V.

Rates of Radical Production from Free Bases.—Attempts to use the oxidation-inhibition method with the unprotonated azoamidines as initiators led to unexpected results. The rates of oxidation initiated by the free bases were unexpectedly slow and, consequently, the inhibition periods were detectable but poorly defined. The rates of uninhibited oxidation with ADMBA, ADMBAH₂⁺⁺ and ABN as initiators were measured and are summarized in Table VI. The low value for the rate of oxidation using ADMBA could conceivably be attributed to inefficient radical production from ADMBA. However, the value of a seemed very low and measurement of the oxidation rate in a mixture containing both ABN and ADMBA (Table VI) showed that the azoamidine inhibits the rate of oxidation initiated by ABN. Obviously the amidine is an oxidation inhibitor of low potency.

 TABLE VI
 INITIATION OF OXIDATION BY ADMBA AT 60°

| ADMBA ₀ , ^a moles × 10 ⁵ | ABN ₀ , ^a moles × 10 ⁵ | ADMBA·2H ₃ ⁺⁺ , ^a moles × 10 ⁵ | R ₀ , moles ^b sec. ⁻¹ × 10 ⁸ |
|--|--|---|---|
| 11.85 | 0 | 0 | 0.68 |
| 0 | 2.71 | 0 | 5.3 |
| 0 | 0 | 2.10 | 17.3 |
| 4.17 | 2.71 | 0 | 0.93 |

^a Amount dissolved in 5 ml. of 2:1 DMSO-tetralin. ^b R₀ = (-dO₂/dt)₀.

There is precedent for the belief that amidines act as oxidation inhibitors.²⁰ Since the oxidation curves obtained with both ABA and ADMBA in the presence of di-*t*-butyl-*p*-cresol showed inhibition periods, although poorly defined, it was possible to make rough estimates of the initiation rates. The value for a calculated for ADMBA was 0.4. A value of 0.4–0.5 was calculated for ABA. Although no high level of confidence can be placed in these numbers, the one for ADMBA is remarkably close to those determined by the method described below.

Since oxidation did not appear to be a suitable reaction for determination of the rates of radical production from neutral azoamidines, we turned to vinyl polymerization. Methyl methacrylate was chosen as the mono-

(20) Danish Patent 64,773 (to A/S Niro Atomizer) (Sept. 9, 1946); *Chem. Abstr.*, **41**, 988a (1947).

(17) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 2457 (1955).

(18) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

(19) P. A. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

mer. Arnett²¹ has previously shown that polymerization of this monomer in the presence of ABN follows the usual rate law, eq. 7.

$$R_p = \frac{k_p[M](ak[RN_2R])^{1/2}}{k_t^{1/2}} \quad (7)$$

where k_p = rate constant for chain propagation and k_t = rate constant for chain termination.

If a series of polymerizations are carried out under identical conditions with two initiators, the relative rates of polymerization can be used to calculate the ratio of the two efficiency factors if the rates of decomposition of the initiators are known.

$$R_{p1}/R_{p2} = a_1^{1/2}(k_1[RN_2R]_1)^{1/2}/a_2^{1/2}(k_2[RN_2R]_2)^{1/2} \quad (8)$$

Table VII summarizes data from polymerization at 69.8° initiated by ABN, ADMBA and ADMBA·2HNO₃. The results indicate that the value of a for ADMBA is 0.67 times that for ABN. Arnett²¹ estimated the a factor for ABN as about 0.6, a value which is quite consistent with efficiencies of the initiator in other solvents. The data indicate that the efficiency of ADMBA is approximately 0.4. A disturbing fact is the value of 0.2 for the efficiency factor for ADMBAH₂⁺⁺ indicated by the data. Since this value is much lower than that obtained from the oxidation

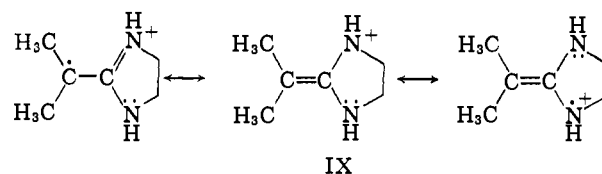
TABLE VII

INITIATION OF POLYMERIZATION OF METHYL METHACRYLATE AT 69.8°

| Initiator | [In] ₀ , moles/l. × 10 ⁴ | R _{p0} , moles/l./sec. × 10 ³ | k _p a ^{1/2} /k _t ^{1/2} ^a |
|-------------------------|---|--|---|
| ABN | 3.25 | 8.39 | 1.010 |
| ABN | 3.25 | 8.31 | 1.001 |
| ABN | 3.25 | 8.68 | 1.046 |
| ABN | 3.25 | 8.66 | 1.044 |
| ADMBA | 2.96 | 5.68 | 0.825 |
| ADMBA | 2.96 | 7.14 ^b | 1.037 |
| ADMBA | 2.96 | 5.45 | 0.792 |
| ADMBA | 1.49 | 4.37 | .893 |
| ADMBA | 1.49 | 4.10 | .837 |
| ADMBA·2HNO ₃ | 1.41 | 12.33 | .610 |
| ADMBA·2HNO ₃ | 1.41 | 12.08 | .597 |

^a Calculated from the equation, $R_p = (k_1^{1/2}[RN_2R])^{1/2}[M] \cdot k_p a^{1/2}/k_t^{1/2}$. Values of k_1 used in the calculations were: ABN, 4.9×10^{-5} sec.⁻¹; ADMBA, 3.7×10^{-5} (from activation energy); ADMBA·2HNO₃, 6.7×10^{-4} sec.⁻¹. ^b Sample known to have become warm during digestion with methanol.

experiments, we suspect that it is in error. A reasonable explanation is found in the hypothesis that amidinium radicals show abnormally low rates of addition to methyl methacrylate and are consequently involved extensively in chain termination. The matter was not further investigated with ADMBA·2HNO₃, but we were concerned that the same phenomenon might be involved in initiation by the neutral amidine. For this reason experiments were carried out using two concentrations of the azoamidine. If inefficient utilization of radicals were involved the apparent value of a should increase as the concentration of initiator is decreased. Although the precision of the results leaves something to be desired, there is no indication that the value of $k_p a^{1/2}/k_t^{1/2}$ varies with initiator concentration. Furthermore, it is not unreasonable that the reactivity of the amidinium radical IX toward methyl methacrylate is exceptionally low. The relatively rapid rate of decomposition of the azobisamidinium salts indicates that rather stable radicals are produced. Furthermore, the fact that the radical bears a positive charge should make it unreactive toward electron-deficient monomers.



Conclusions.—There seems to be little doubt that there is significant inefficiency in the production of “free” radicals in the decomposition of bisazoamidinium salts. We attribute the inefficiency to geminate recombination of the cation radicals formed in the primary decomposition process. Although there is more than usual uncertainty in the measurements of the efficiencies of radical production from the neutral azoamidines, it seems fairly certain that the efficiencies of these compounds are somewhat lower than those of the second conjugate acids. The difference between the values for the salts and the free bases could be attributed to reduction of the coupling rate because of electrostatic repulsion between the radicals. However, even this conclusion is by no means firm. Comparison of the rates of decomposition of the azo compounds indicates that the cation radicals are more stable than their neutral analogs; this factor alone could reduce the extent of geminate coupling. The efficiency factors are summarized in Table VIII.

We suggest that in any solvent in which second conjugate acids can be formed, enough of the positive charges, formally borne by the radicals, will be dispersed into the solvent to allow coupling to occur with high rates.

TABLE VIII

EFFICIENCY OF RADICAL PRODUCTION FROM AZOAMIDINES AND THEIR SALTS

| Azo compound | Method of measurement | a |
|-------------------------|-----------------------|-----------------|
| ABA | Oxid. inhibition | 0.45 ± 0.05 |
| ABA·2HNO ₃ | Oxid. inhibition | 0.60 |
| ADMBA | Oxid. inhibition | .4 |
| ADMBA | Vinyl polymn. | .4 |
| ADMBA·2HNO ₃ | Oxid. inhibition | .66 |

Experimental

Materials.—Dimethyl sulfoxide (DMSO), Crown-Zellerbach technical grade, was purified in the following manner. After a preliminary distillation at reduced pressure the distillate was shaken with Linde Co., Type 4A, Molecular Sieve. The dry DMSO was filtered through Celite in a dry-box under an atmosphere of dry nitrogen and redistilled at 0.2 mm. through a 12-in. Vigreux column. A center fraction boiling at 45° was collected for use. Cumene, Matheson, Coleman and Bell, was shaken with portions of concentrated sulfuric acid in a separatory funnel until the acid layer was not decolorized. The material was then washed with several portions of water and dried over anhydrous magnesium sulfate. The solvent was then distilled at reduced pressure (20 mm.) and the center fraction distilling over the range 49–50° was collected for use. Tetralin was purified in the same manner as cumene. The tetralin used in these studies was obtained from Dr. L. Mahoney. Methyl methacrylate (MMA) was purified according to the method of Arnett.²¹ The purified monomer was stored in a tightly sealed brown bottle in the refrigerator. Azobisisobutyramidinium chloride (ABA·2HCl) was obtained from the Yerkes Research Laboratory, E. I. du Pont de Nemours Co., Buffalo, N. Y. The chloride was recrystallized from water before use in kinetic experiments. Azobisisobutyramidinium nitrate (ABA·2HNO₃) was prepared from the chloride by addition of an equivalent amount of aqueous silver nitrate. The silver chloride was filtered off and the nitrate was precipitated by addition of a large quantity of acetone and recrystallized from ethyl alcohol; m.p. 162° dec. Anal. Calcd. for C₈H₂₀N₂O₆: C, 29.63; H, 6.22; N, 34.55. Found: C, 29.75; H, 6.30; N, 34.45.

Azobisisobutyramidine (ABA).—In a typical experiment, 9.2 g. (0.4 mole) of sodium was added to 300 ml. of dry methanol (previously distilled from magnesium). After all the sodium had dissolved, a 54.2-g. (0.2 mole) sample of ABA·2HCl was added to the methanol solution. During addition of the chloride, and for 1 hour thereafter, the solution was stirred with a magnetic

(21) L. M. Arnett, *J. Am. Chem. Soc.*, **74**, 2027 (1952).

stirrer. The solution was then filtered through a sintered glass funnel, and the clear yellow filtrate was evaporatively distilled under aspirator vacuum at 35°. The residual solid material was added to 400 ml. of chloroform and the solution was filtered. The yellow chloroform filtrate was evaporatively distilled at 35° under aspirator vacuum, and the resulting solid was dried *in vacuo* over phosphorus pentoxide and recrystallized from methanol; m.p. 139° dec. *Anal.* Calcd. for C₈H₁₂N₆: C, 48.46; H, 9.15; N, 42.39. Found: C, 48.20; H, 9.30; N, 42.55. A sample of recrystallized material was added to 1 *N* hydrochloric acid. Upon addition of acetone to this solution, a solid was isolated which gave an infrared spectrum (Nujol mull) identical with authentic ABA·2HCl. An ultraviolet spectrum of a solution (2.78 10⁻² M) of ABA in DMSO exhibited the characteristic azo absorption; λ_{max} 3700 Å., ε 30 liter mole⁻¹ cm.⁻¹.

Azobis-N,N'-dimethyleisobutyramidine (ADMBA).—A 10-g. sample of ABA·2HCl was dissolved in 100 ml. of 98% ethylenediamine with stirring at room temperature. After a few minutes a white solid precipitated. The solid was separated by filtration and recrystallized first from chloroform and then from dry methyl alcohol; m.p. 122.5° dec. *Anal.* Calcd. for C₁₂H₂₄N₆: C, 57.56; H, 8.86; N, 33.57. Found: C, 57.65; H, 8.97; N, 33.46. The bisamidinium chloride was prepared by passing anhydrous hydrogen chloride through a chloroform solution of the free base. *Anal.* Calcd. for C₁₂H₂₄N₆Cl₂: C, 44.58; H, 7.49; N, 26.00; Cl, 21.94. Found: C, 44.48; H, 7.51; N, 25.88; Cl, 21.86. The bisamidinium nitrate was prepared by addition of an equivalent amount of concentrated nitric acid to a solution of the free base in ethyl alcohol. The precipitate was removed by filtration and recrystallized from water; m.p. 146.5° dec. *Anal.* Calcd. for C₁₂H₂₄N₆O₆: C, 38.29; H, 6.43; N, 29.77. Found: C, 38.27; H, 6.29; N, 29.82. Thermal decomposition of the salt in DMSO yields the calculated amount of nitrogen.

Tetramethylsuccinodinitrile.—A 165-g. sample of azobisisobutyronitrile was dissolved in 1300 ml. of carbon tetrachloride. Dry nitrogen was bubbled through the solution for 15 minutes. The inlet tube was sealed off and the flask and contents were heated at reflux with continuous stirring for 48 hours. The solvent was evaporatively distilled at room temperature under reduced pressure until a crystalline mush remained in the flask. The residue was filtered on a coarse sintered glass funnel and the resulting white solid was dried at room temperature to give 113.4 g. (84% yield) of product, m.p. 114–125°. The solid was sublimed at 80° under aspirator vacuum and white crystals were obtained, m.p. 153–158°. Recrystallization of this material from petroleum ether gave crystals, m.p. 166–167°.

Tetramethylsuccinic Anhydride.—A 25-g. sample of TMSN was hydrolyzed in 100 ml. of 80% sulfuric acid according to the method of Thiele and Heuser.²² The product was obtained in 87% yield.

Tetramethylsuccinimide (TMSI). was prepared according to the method of Auwers and Gardner²³; yield 83%. The imide, twice sublimed at 90° (2 mm.), gave white crystals, m.p. 186.8–187.8° (lit. m.p. 187°). An infrared spectrum of TMSI showed two carbonyl absorptions at 1730(s), and 1785(m) cm.⁻¹.

Thermal Decomposition of ABN in DMSO.—A 5.0-g. sample of ABN was dissolved in 100 ml. of DMSO. Dry nitrogen was passed through the solution for 3 minutes. The solution was heated at approximately 70° for 39.5 hours with continuous stirring. The yellow reaction mixture was continuously extracted with pentane for 20 hours. At the end of this period two layers were observed in the receiver flask. The pentane layer was evaporated and yielded 0.1 g. of solid material which was sublimed at 90° (745 mm.) giving pure white crystals; 20 ml. of water was added to the second layer. A solid material precipitated from solution and was filtered off; weight 1.8 g. This DMSO–water solution was further extracted with several portions of pentane in a separatory funnel. Evaporation of the pentane (500 ml.) gave 0.5 g. of a solid.

The remaining 80 ml. of the original reaction mixture was removed from the extraction apparatus and 100 ml. of water was added to it. The solution became cloudy, but no detectable amount of precipitate was obtained. This aqueous DMSO solution was continuously extracted with pentane for 44 hours. The pentane layer was evaporated and 1.1 g. of solid material was isolated. The aqueous DMSO layer was then shaken with several portions of pentane in a separatory funnel. Evaporation of the pentane yielded 0.3 g. of white crystals.

The total weight of solid material isolated was 3.7 g. (89% yield). This was shown to be tetramethylsuccinodinitrile by comparison of its infrared spectrum with that of authentic material. The solid was sublimed twice at 90° (745 mm.). No significant amount of residue remained after sublimation. This sublimed material had a m.p. of 150–155°. Authentic TMSN which had been sublimed had a m.p. of 153–158°.

Thermal Decomposition of ABA·2HNO₃ in DMSO.—A 1.5-g. sample of ABA·2HNO₃ was dissolved in approximately 25 ml. of anhydrous DMSO and dry nitrogen was bubbled through the solution for approximately 30 minutes. The nitrogen inlet tube was then sealed off and the flask was immersed for 30 minutes in an oil-bath pre-heated to approximately 100°. Nitrogen evolution was observed only during the first 15 minutes of reaction. The reaction mixture was evaporatively distilled at reduced pressure leaving a light yellow solid. The distillate had an ammoniacal odor. The solid was washed with anhydrous ether and the washings were discarded. The solid material was then dissolved in anhydrous methanol and the methanolic solution was heated and filtered to remove trace insoluble impurities. This solution was then concentrated with stirring under a vacuum bell jar at reduced pressure (~135 mm.) until solid material began to precipitate. The flask containing this solution was stoppered and placed in the refrigerator for 24 hours. The solid material was filtered from solution on a sintered glass funnel and dried *in vacuo*; weight of this material is 0.35 g., m.p. 293–297°, yield based on the empirical formula 35%. *Anal.* Calcd. for tetramethylsuccinimidinium nitrate, C₈H₁₆N₄O₃: C, 44.43; H, 7.46; N, 25.91; O, 22.20. Found: C, 44.52; H, 7.58; N, 24.84.

A 0.2-g. sample of this salt and 20 ml. of a 16% sodium hydroxide solution were placed in a 50-ml., single neck, round-bottom flask fitted with a reflux condenser. The solution was heated at reflux with continuous stirring for 48 hours. The reaction mixture was acidified with 6 *N* hydrochloric acid and a solid precipitated from solution. The solid and water layer were extracted with two 200-ml. portions of ether and the combined ether extracts were evaporated. A yellow oily residue remained which crystallized upon further evaporation *in vacuo*. An infrared spectrum of the crude solid product was identical with that of an authentic sample of tetramethylsuccinimide.

Thermal Decomposition of ADMBA·2HNO₃ in DMSO.—A 2.0-g. sample of ADMBA·2HNO₃ was dissolved in 25 ml. of DMSO. The reaction vessel containing the solution was immersed in an ice–water-bath and degassed. The solution was then allowed to thaw to room temperature *in vacuo*. The outlet of the vessel was connected to a mineral oil bubbler. Dry nitrogen was bubbled through the solution for several minutes after the degassing procedure. The vessel was then heated at 70° for 3 hours. Solvent was then removed by evaporation at 45° (1 mm.) leaving a smooth caramel-colored mush weighing 2.21 g. A 10-ml. portion of absolute ethyl alcohol was added to the residue, giving a white solid and a yellow solution. The solid was separated by filtration and washed with absolute ethyl alcohol and the solid was dried over phosphorus pentoxide. The weight of the solid was 0.54 g., yield based on the empirical formula 29.2%. This material chars at 217°, and melts at ~225° with decomposition. *Anal.* Calcd. for bis-N,N'-dimethylenetetramethylsuccinamidinium nitrate, C₁₂H₂₄N₆O₆: C, 41.37; H, 6.94; N, 24.13; O, 27.56. Found: C, 41.36; H, 6.80; N, 24.05. An n.m.r. spectrum of this material in deuterium oxide shows two sharp singlet resonances at 85 and 240 c.p.s. (60 Mc.p.s.; reference, tetramethylsilane, external) in the ratio 12:8. A proton signal for water is visible at 282 c.p.s. An n.m.r. spectrum of ADMBA·2HNO₃ in deuterium oxide shows two sharp singlets at 94 c.p.s. and 245 c.p.s. in the ratio 12:8. These are identified as CH₃–C– and N–CH₂–C protons, respectively. The water resonance signal is found at 283 c.p.s. The infrared spectra (Nujol mull) of ADMBA·2HNO₃ and the solid product are almost identical. Each possess the characteristic bands at: C–N stretch, 1750 c(w), 1600(s) and 1460(s)cm.⁻¹; a broad nitrate ion band at 1400–1250 cm.⁻¹. The fingerprint regions are superimposable with only minor variations.

In a second reaction, a 2.0-g. sample of ADMBA·2HNO₃ was dissolved in 20 ml. of DMSO and decomposed in the same manner as described above. The resultant reaction mixture was evaporated until only 2–3 ml. of solvent remained. To this solution was added 10 ml. of 20% sulfuric acid. The resultant solution was divided into two parts, each of which was placed in a tube with a constricted neck. The tubes were sealed and immersed in an oil-bath at 78° for 5 days. At the end of this period, the tubes were opened and the combined contents extracted with several portions of ether totaling 100 ml. The ether layer was dried over magnesium sulfate and evaporated to a total volume of 1–2 ml. The resultant ether solution was orange and smelled very much like isobutyric acid. A preliminary analysis of this ether solution was done by vapor phase chromatography, using a 7-ft. Carbowax 20 M column at 160° in an Aerograph Corp. vapor phase chromatography instrument. The majority of the peaks were broad and exhibited marked tailing. Retention times for the components are referred to the ether peak. The chromatograph indicated components having retention times of 1.7, 3.2, 9.9, 19, 23.5 and 34.3 min. A sample of authentic isobutyric acid and tetramethylsuccinic anhydride in ether gave three peaks. Retention times based on the ether peak are 17.3 and 36.5 min. for the acid and anhydride, respectively. A sample of isobutyric acid and the reaction mixture were mixed. The peak giving the re-

(22) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(23) K. Auwers and J. A. Gardner, *Ber.*, **23**, 3622 (1890).

tention time of 19 min. in the reaction mixture increased in size in comparison to the other peaks.

Thermal Decomposition of ADMA in DMSO.—A 6.8-g. sample of ADEBA in 200 ml. of DMSO was flushed with dry nitrogen and heated at 90° for 3 hours. The reaction mixture was concentrated to approximately 100 ml. by evaporative distillation at reduced pressure. The solution was filtered and the solid was washed with ether and dried *in vacuo* over phosphorus pentoxide; weight 1.50 g. This solid was dissolved in excess chloroform and filtered to remove small amounts of insoluble impurities. The chloroform solution was concentrated until solid began to precipitate from solution and was then placed in the refrigerator. The solid was filtered from solution and dried over phosphorus pentoxide *in vacuo*; softens at 171°, m.p. 174–176°.

An n.m.r. spectrum was taken of a solution of this solid in chloroform. This spectrum is complex and has not been analyzed. The spectrum showed the following resonances: sharp singlets at 72 and 75 c.p.s., a weak singlet at 82 c.p.s., and a broad singlet at 92.5 c.p.s. The region between 165 and 275 c.p.s. shows a series of complex multiplets. Proceeding downfield, the first multiplet appears at first glance to be a triplet; however, the three signals have maxima at 172.5, 177.5 and 184 c.p.s. The central signal has a shoulder at about 178–179 c.p.s. indicating that the multiplet might be composed of two superimposed doublets centered at 175.5 and 180.5 c.p.s. ($J \approx 6$ c.p.s.). A similar multiplet is visible further downfield with maxima at 209, 215 and 220 c.p.s. Again, a shoulder on the central signal at approximately 213 c.p.s. is visible. This could correspond to two superimposed doublets with $J \approx 6$ c.p.s. The next multiplet consists of 8 resolvable components at 226 and 231.5 c.p.s. (minor); 238.5, 245, 250 and 256.5 c.p.s. (major); and 268.5 and 273.5 c.p.s. (minor). The components designated as minor are considered to arise from a different compound from that corresponding to the major components. The major components exhibit fine structure which may be second-order splitting, or due to overlap of more complicated multiplet patterns. Integration gives the following results: the ratio of the protons giving signals between 0 and 100 c.p.s. to those giving the complicated multiplet patterns from 150–275 c.p.s. is 31.1 to 17.7 or approximately 14 to 8. The broad singlet at 92.5 c.p.s. accounts for 2.2 of the 14 protons in the region 0–100 c.p.s. The complex multiplet consisting of 8 components accounts for 3.7 protons in the region 150–275 c.p.s., and the two "triplet" patterns at ~215 and ~177 c.p.s. account for 2.2 and 2.0 protons, respectively. The n.m.r. spectrum of ADMBA in chloroform gives a very simple spectrum consisting of a sharp singlet at 881 c.p.s. and a broad singlet at 221 c.p.s. which are in the ratio 14 to 8.1 by electronic integration. The higher field singlet has a small shoulder on the low field side. It is assumed that the higher field signal corresponds to the C-CH₃ and N-H protons while the lower field signal is due to the C-CH₂-N protons.

The n.m.r. spectrum of the unknown solid material in 15% sulfuric acid is extremely simple. The solvent signal, which obscures the region immediately below 300 c.p.s., and only two other sharp singlets are observed at 94 and 248 c.p.s. in the ratio of 1 to 7.2, respectively. The n.m.r. spectrum of ADMBA in 15% sulfuric acid gives two sharp singlets at 98 and 249 c.p.s. in the ratio 12 to 8.0, respectively. The signals for ADMBA are identified as the C-CH₃ protons and the C-CH₂-H protons, respectively.

The infrared spectra of both the unknown solid product and ADMBA differ considerably. A sharp band present at 3430 cm.⁻¹ in the spectrum of ADMBA is absent in the unknown. The unknown shows strong bands at 1700 and 1650 cm.⁻¹, while ADMBA shows a single strong band at 1625 cm.⁻¹. The band at 1625 cm.⁻¹ for ADMBA exhibits a weak shoulder at about 1560 cm.⁻¹, while the band at 1650 cm.⁻¹ for the unknown has a slightly more pronounced shoulder at 1575 cm.⁻¹. A broad band from 1410–1425 cm.⁻¹ is present in both spectra, but more intense for ADMBA. The unknown shows moderately strong bands at 1375 and 1300 cm.⁻¹; while ADMBA possesses a weaker doublet (1375 and 1360 cm.⁻¹) and an intense broad band at 1275 cm.⁻¹. The remainder of the fingerprint regions in each spectrum are practically superimposable.

Further concentration of the DMSO filtrate (45° (1 mm.)) using a rotary evaporator gave 0.5 g. of solid material which gave an n.m.r. spectrum in chloroform identical with that of the first isolated solid. The total yield of solid material based only on loss of nitrogen from ADMBA is 33.6%.

The residual reaction mixture consisted of a viscous dark orange liquid. An n.m.r. spectrum was taken of this crude material in chloroform. The region of 50–100 c.p.s. is quite complicated, consisting of a series of closely spaced signals at 70, 73.5, 77, 80, 81.5, 86, 88 and 93 c.p.s. The DMSO solvent signal appears at ~162 c.p.s. and two strong singlets at 220 and 223 c.p.s. are present. A broad singlet is also present at 345 c.p.s. The signals given above are almost as intense as the solvent signal, indicating that the viscous orange liquid still contains a large concentration of products. An infrared spectrum of a chloroform solution of this orange liquid appears to be a superposition of the spectra for the unknown solid and ADMBA.

Measurement of Rates of Nitrogen Evolution.—The rate of gas evolution was monitored manometrically. Constant pressure was maintained by means of a mercury reservoir which was raised or lowered by a spindle driven by an electric motor. The motor was activated by a relay which was in turn controlled by a thermocap (Niagara Electron Laboratories) clamped onto a reference mercury manometer. Changes in gas volumes were measured with gas burets sealed into the system. The temperature of the reaction vessel was controlled by circulating water from a constant temperature bath through an outer jacket surrounding the reaction chamber. The solutions were stirred by a Teflon enclosed magnetic bar driven by a magnetic stirrer. Before rates of nitrogen evolution were measured, the system is evacuated and refilled with nitrogen three times. The apparatus is very sensitive and gives excellent results in runs in which the total change in gas volume is 5 ml.

Attempts to Remove Ammonia from Gas Evolved from ABA.—

(a) A vessel was modified in the following manner. An additional length of glass tubing was added above the reflux condenser. This section was thermostated by the condenser water jacket. A plug of glass wool was inserted into this tube so that it rested at the point where the top of the condenser was attached to the bottom of this tube. Fine boiling chips which had been soaked in sulfuric acid were then poured onto the glass wool plug in sufficient amount to fill the tube. A 0.200-g. sample of ABA was placed in the gas reaction vessel and 5 ml. of DMSO was added. The rate of gas evolution was monitored giving a rate constant $k = 5.0 \times 10^{-6}$ sec.⁻¹.

(b) The modified gas apparatus reaction vessel described in (a) was used. Instead of filling the tube with boiling chips, fine crystals of *p*-toluenesulfonic acid monohydrate were used. A layer of Drierite and a plug of glass wool were placed on top of the acid crystals. A 0.2017-g. sample of ABA and 5 ml. of DMSO were added to the reaction vessel. The rate of gas evolution at 70° was monitored giving a rate constant $k = 2.6 \times 10^{-6}$ sec.⁻¹.

(c) A second reaction vessel containing concentrated sulfuric acid was connected to the thick-walled capillary manifold of the gas apparatus between the normal reaction vessel and the first gas buret. A 0.02153-g. sample of ABA and 5 ml. of DMSO were placed in the reaction cell. The rate of gas evolution at 70° was monitored giving a rate constant of 3.2×10^{-6} sec.⁻¹.

Ammonia Evolution from ABA.—A 2.0035-g. (0.0101 mole) sample of ABA was dissolved in 50 ml. of DMSO. The reaction vessel was designed so that nitrogen gas could be passed through the solution and out of the vessel during a decomposition run. A piece of Tygon tubing connected the outlet of the reaction vessel to a 600-ml. beaker fitted with a large rubber stopper containing five holes. Two of the holes were fitted with Beckman glass and calomel electrodes. The third hole was fitted with the tip of a micro-buret, the fourth with a sintered glass gas dispersion tube, and the fifth was used as a gas outlet. The beaker was filled with sufficient water to cover the electrodes and the gas dispersion tube. The electrodes were connected to a Beckman model G pH meter and the reaction vessel was immersed in a thermostated oil-bath, regulated at 70°. Dry nitrogen gas was passed simultaneously through, and above, the reaction mixture. A known volume of standardized 0.0968 *N* hydrochloric acid was added to the water solution in the second vessel. The pH of the solution was recorded as a function of time. When the pH of the solution reached approximately 7, another aliquot of acid was added to the solution. No detectable amount of ammonia escaped from the water solution. Plots of pH vs. time were made, and the time interval between two identical pH readings (normally pH 6.2–6.6) gave the time required for the evolving ammonia to neutralize the known amount of added acid. The average rate of ammonia evolution over this given time interval was then calculated. The data are presented in Table IX.

Oxidation rates were measured with either the same apparatus used for study of rates of nitrogen evolution or with the apparatus described earlier.²⁴

Polymerization of Methyl Methacrylate.—A weighed sample of the initiator was placed in a 25-ml. volumetric flask and dissolved in sufficient DMSO to bring the solution to volume. After the solution was thoroughly mixed, a 5.0-ml. aliquot of each DMSO solution was pipetted into a 50-ml. volumetric flask. The flask was stoppered and weighed. Sufficient purified methyl methacrylate was then added to each flask to bring the solution to volume. The flasks were again stoppered and weighed. The concentration of monomer was determined from the weight difference. Ten-ml. aliquots were taken from each 50-ml. flask and transferred to 18 × 150 mm. culture tubes (Kimble) which had been constricted near the top. The tubes were immediately attached to a vacuum manifold and degassed by four freeze-thaw cycles (freezing in a slurry of solid carbon dioxide and isopropyl alcohol). The tubes were sealed off under vacuum and allowed to warm to room temperature. All of the tubes were

(24) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen. *J. Am. Chem. Soc.*, **77**, 3233 (1955).

TABLE IX

RATE OF EVOLUTION OF AMMONIA FROM ABA IN DMSO AT 70°

| Reaction time, hr. ^a | Δ , min. | Equiv. acid added $\times 10^5$ | $d\text{NH}_3/dt \times 10^5$ ($R \times 10^5$), equiv./hr. |
|---------------------------------|-----------------|---------------------------------|---|
| 103.56 | 28.5 | 1.94 | 4.08 |
| 104.13 | 38.3 | 2.90 | 4.55 |
| 104.66 | 26.7 | 1.94 | 4.35 |
| 122.50 | 30.1 | 1.94 | 3.86 |
| 123.03 | 29.7 | 1.94 | 3.91 |
| 123.57 | 30.6 | 1.94 | 3.80 |
| 125.58 | 31.7 | 1.94 | 3.66 |
| 126.21 | 47.1 | 2.90 | 3.70 |
| 126.88 | 31.0 | 1.94 | 3.75 |
| 147.00 | 35.2 | 1.94 | 3.30 |
| 147.58 | 35.0 | 1.94 | 3.32 |
| 148.18 | 36.1 | 1.94 | 3.22 |
| 148.82 | 35.7 | 1.94 | 3.25 |
| 195.18 | 47.8 | 1.94 | 2.43 |
| 196.37 | 94.8 | 3.87 | 2.45 |

^a The reaction time refers to the total time of reaction corresponding to the rate of ammonia evolution listed in the fourth column. It is an average value of the reaction times at the beginning and end of a given neutralization. Data prior to the 103-hour reaction time have been obtained but there is extremely large scatter due to poor experimental technique.

then simultaneously placed in a constant temperature bath regulated at 69.8°. An initial drop in temperature of 0.4° was noted. The bath re-equilibrated in less than 7 minutes. After a predetermined length of time the tubes were removed from the bath and immediately quenched by cooling with ice-water, and then immersed in a slurry of carbon dioxide in isopropyl alcohol.

The total length of time (to the nearest minute) from initial immersion of the tubes in the constant temperature bath, to quenching in ice-water, was taken to be the reaction time. The tubes were stored in solid carbon dioxide in the dark until analysis was performed. Analyses were carried out within 2 days of the kinetic run.

A typical analysis for polymer content will be described. The tube was warmed to room temperature and carefully broken open. Previously, a Waring blender had been filled with approximately 500 ml. of absolute methyl alcohol. The speed of the blender was controlled by a Variac. The alcohol solution was stirred at a moderate speed and the contents of the tube were rapidly, but carefully, poured into the blender. The tube was washed with several small portions of benzene and the washings were transferred to the blender. When all of the reaction mixture had been transferred, the blender speed was increased and the heterogeneous mixture was stirred for 4–5 minutes. The supernatant liquid and solid flocculent polymer were rapidly transferred to a 1-liter erlenmeyer flask with the aid of a large powder funnel taking care to avoid loss of polymer due to seepage of liquid down the side of the blender container. The sides of the blender container were scraped with a spatula while a stream of methanol was directed on them to remove a small amount of residual polymer. These washings were transferred to the 1-liter erlenmeyer flask. The funnel was also carefully washed. The heterogeneous mixture in the flask was then filtered through two dry and preweighed sintered glass crucibles with the aid of an aspirator vacuum. The flask was rinsed with several washings of methyl alcohol and these were passed equally through the two crucibles. The crucibles were covered with filter paper and allowed to stand at room temperature for several hours. The crucibles were then dried in an oven at 70° for 45 minutes, allowed to cool and weighed.

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Mechanisms of Acid-catalyzed Reaction. IV.¹ The Kinetics of Ring Opening of Styrene Episulfide

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The kinetics of styrene episulfide ring opening have been studied in various solvent media and over a wide range of acid strengths. Similar studies on styrene epoxide appear to fail because of a competing rearrangement reaction. The rate data from runs in water-alcohol solutions have been correlated with the S.-C. criterion,^{1a} providing a basis for concluding that an A1 mechanism does not prevail under these conditions. The corresponding data in purely aqueous solutions, however, when correlated by means of the *w* and Z.-H. criteria⁹ appear to suggest to the contrary. Some attempt has been made to reconcile these contradictions and to unify the conclusions which are obtainable when the S.-C. and *w* criteria are concurrently applied.

Introduction

One of the general objectives of our program of study is to establish the nature and extent of differences in reactivity introduced by substitution of a sulfur for an oxygen atom in analogous structures. The results we are reporting here were obtained in the effort to characterize the acid-catalyzed episulfide ring opening reaction for comparison with the corresponding epoxide reaction.

Pritchard and Long have studied the kinetics of solvolysis of ten epoxides in aqueous perchloric acid.^{2a} On the basis of these and related studies^{2b–c} these authors have concluded that an A1 mechanism (rate-determining unimolecular ring opening of the conjugate substrate acid) prevails. The keystone in their argument is their finding^{2a} that $\log k$ is proportional to $-H_0$ in every case, consistent with the Zucker-Hammett (Z.-H.) criterion.³ However, this conclusion has been disputed

in several cases on the basis of other criteria which suggest that the reaction of the conjugate substrate acid with hydroxylic solvent is rate determining.⁴ Recently, also, Bunnett has developed an empirical criterion for acid-catalyzed mechanism in aqueous solution⁵ which, when applied to the data of Pritchard and Long,^{2a} appears to support the nucleophilic participation of water in the slow step of epoxide hydrolysis.^{5d}

In our approach to the study of the analogous episulfide ring opening reaction we have also sought to compare deductions reached by means of several mechanistic criteria with the purpose of determining, if possible, where the limitations may lie in the application of each. Thus, it was necessary to examine reaction rates over a range of ethanol-water and acid concentrations in order to apply the solvent composition criterion.^{1a} Data obtained for the reaction rates in aqueous solutions as a function of concentrations varying

(1) For previous papers in this series see: (a) H. Kwart and L. B. Weisfeld, *J. Am. Chem. Soc.*, **80**, 4670 (1958); (b) H. Kwart and A. L. Goodman, *ibid.*, **82**, 1947 (1960); (c) H. Kwart and M. B. Price, *ibid.*, **82**, 5123 (1960); (d) H. Kwart and J. A. Herbig, *ibid.*, **85**, 226 (1963).

(2) (a) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 2667 (1956); (b) **78**, 6008 (1956); (c) **79**, 2365 (1957); (d) **80**, 4162 (1958); (e) F. A. Long, J. G. Pritchard and F. E. Stafford, *ibid.*, **79**, 2362 (1957).

(3) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

(4) See ref. 1b and J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959), for the detailed treatments which dispute the A1 mechanism proposed.^{2a}

(5) (a) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961); (h) **83**, 4968 (1961); (c) **83**, 4973 (1961); (d) **83**, 4978 (1961).