[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Evidence of Partial Failure of the Br^{80} Isomeric Transition to Rupture Carbon–Bromine Bonds[1]

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The efficiency of the Br^{80m}(4.4 hr.) → Br^{80} (18 min.) isomeric transition in breaking the carbon–bromine bond has been determined for five organic bromides. It is found to be less than 100% in four of the cases and to be determined in part by the substituents on the carbon atom and in part by whether the compound is in the liquid or gas phase. The approximate values for failure to rupture are: CCl_3Br_{gas}, 7%; CH_3Br_{gas}, 6%; CF_3Br_{gas}, 1%; CCl_3Br in liquid bromine, 13%; CH_3Br in liquid bromine, 6%; C_6H_5Br in liquid bromine, 13%.

Introduction

When Br^{80m} (4.4 hr. half-life) undergoes isomeric transition to the lower nuclear energy state, Br^{80} (18 min. half-life), part of the energy is always lost in ejecting a K- or L-electron from the atom (internal conversion),[2,3] thus leaving a positively charged bromine ion.[4] The positive charge may be increased by several units as the result of emission of Auger electrons instead of X-rays.[5] The conversion electrons from the isomeric transition do not impart sufficient recoil energy to the atom to be chemically significant[6] but the positive bromine ion usually splits out of its parent compound[6a,7,8] either because of the chemical instability resulting from loss of its binding electrons, or because of coulombic repulsion following distribution of the charge over the whole molecule, or because of the energy made available by the charge neutralization process.

It is important to seek further evidence on this phenomenon because: (1) of the interest in the internal conversion and Auger processes *per se;* (2) of the information which it can give on the stability of positively charged molecular ions and on the chemical effects of charge neutralization processes; (3) it utilizes a process of chemical activation which is independent of temperature and therefore is a useful tool for the study of phase effects on chemical reactions.

Several lines of indirect evidence have suggested that organically bound Br^{80} which undergoes isomeric transition in the liquid or solid phase may, in part, remain in combination with its original organic radical partner.[9] This could be due either to failure of the transition to rupture the C–Br bond or to primary recombination within the parent cage.

In order to obtain more conclusive evidence about the degree of retention of the transition daughter in the parent compound, we have determined the organic yields for the transition in CCl_3-Br^{80} and related compounds when present at low concentration in both liquid and gaseous bromine. Under such conditions any Br^{80} (18 min.) atom which is split from its parent radical by the transition and which escapes primary combination in the parent cage has negligible chance to re-enter organic combination.

Experimental

General Procedure.—Br^{80m} (4.4 hr.)[10] was introduced into each of the compounds to be tested by methods described below. A sample of the tagged compound was then allowed to stand in the presence of a many-fold excess of inactive bromine for at least ten half-lives of the Br^{80} (18 min.) daughter. At the end of this period essentially the only Br^{80} (18 min.) activity present was that which was formed during the standing period. Those Br^{80} (18 min.) atoms which broke the carbon–bromine bond as a result of the isomeric transition were in inorganic form, having exchanged with the excess of bromine molecules in the system. Those which failed to break the parent bond and escape from the parent radical were in organic combination. The elemental bromine was usually separated from the organic compound by transfering the mixture rapidly, on a vacuum system, through a tube of finely divided copper (which was shown to remove inorganic bromine quantitatively), to a 20-ml. annular jacket surrounding the sensitive portion of a thin walled glass Geiger tube. This was done by cooling a side-arm on the Geiger tube jacket with liquid air and opening the stopcocks connecting the jacket to the reaction flask, through the copper train. While the organic vapor was condensed the tube jacket was sealed off from the vacuum line with a flame. The condensed compound was then revaporized, and counting was started in 1.5 minutes or less from the start of the separation. Under the conditions used for counting, the radiations from Br^{80m} (4.4 hr.) were not detectable so the observed counting rate was due wholly to Br^{80} (18 min.) which failed to escape from its parent organic radical following the isomeric transition, plus Br^{80} (18 min.) which grew in following the separation of the elemental bromine. In order to determine the fraction of the total Br^{80} (18 min.) which was in organic form at the time of separation, one minute counts were taken every two minutes until the maximum of the growth curve had been reached (Fig. 1), and continued at longer intervals after the counting rate was controlled by the 4.4 hour half-life of the parent of the isomeric transition. Later counts were taken to establish the Br^{82} (36 hr.) content of the mixture, and the earlier counts were corrected for this background, which was usually less than 10% of the counting rate of all of the bromine in the reaction mixture before separation. A small experimentally determined correction for coincidence loss in counting was also applied. Extrapolation (Fig. 1) of the 4.4 hour decay curve back to the time of separation of the elemental bromine from the organic compound gave the counting rate of the Br^{80} (18 min.) present in equilibrium with the Br^{80m} (4.4 hr.) in the reaction mixture at that time.

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[1] Presented, in part, before the Nuclear Chemistry Section of the XII International Congress of Pure and Applied Chemistry in New York, Sept., 1951.

[2] A. D. Grinberg and L. I. Rossinow, *Phys. Rev.*, **58**, 181 (1940).

[3] P. Rothwell and D. West, *Proc. Phys. Soc. (London)*, **A63**, 539 (1950).

[4] S. Wexler and T. H. Davies, *J. Chem. Phys.*, **18**, 376 (1950).

[5] (a) E. P. Cooper, *Phys. Rev.*, **61**, 1 (1942); (b) S. Wexler, abstracts of papers presented at the Atlantic City Meeting of the American Chemical Society, Sept., 1952, page 33P.

[6] (a) J. E. Willard, THIS JOURNAL, **62**, 256 (1940); (b) G. T. Seaborg, G. Friedlander and J. W. Kennedy, *ibid.*, **62**, 1309 (1940).

[7] L. LeRoux, C. Lu and S. Sugden, *Nature*, **143**, 518 (1939).

[8] W. H. Hamill and J. A. Young, *J. Chem. Phys.*, **17**, 215 (1949).

[9] S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2273 (1951).

[10] Radiobromine was obtained in some cases by irradiating ampoules of liquid bromine in the pile at the Argonne National Laboratory. In other cases it was produced by irradiating alkyl bromides with neutrons from an antimony-beryllium source obtained from the Oak Ridge National Laboratory, and separating the high specific activity product of the Szilard-Chalmers process.

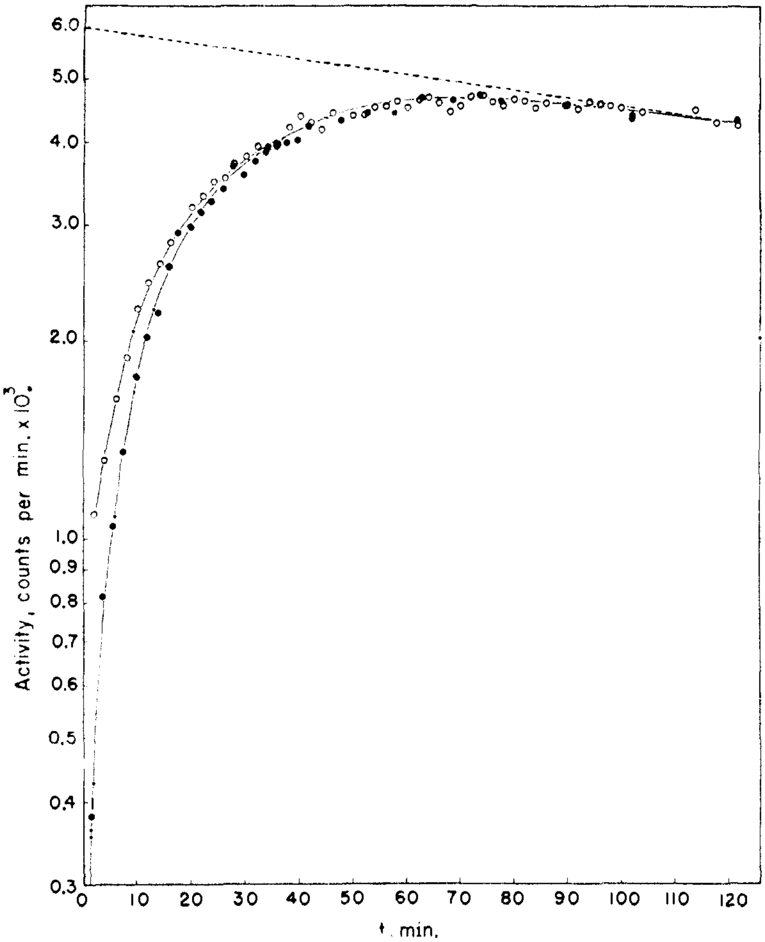

Fig. 1.—Typical growth of Br^{80} (18 min.) activity in organic bromide gas immediately following separation of elemental bromine: O, CCl_3Br gas experiment, 8.8% retention; ●, CF_3Br experiment, 0.1% retention; lower curved line calculated for 0% retention. In this plot the two experimental curves have been normalized to the same value of I_2^0 at 0 time, *i.e.*, 6000 c./m.

The counting rate in the organic compound at that time could, in principle, be determined by extrapolation of the experimental growth curve to the time of separation. Since accurate extrapolation was difficult because the slope of this curve was steep and rapidly changing the value ($A_2°$) was calculated from each of the first four points on the curve. The results, which were usually in good agreement, were averaged. Calculation was made by the expression

$$A_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1} A_1{}^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + A_2{}^0 e^{-\lambda_2 t}$$

in which A, λ and t represent the activity in organic combination, decay constant and time, respectively. The subscript "1" refers to Br^{80m} (4.4 hr.) and "2" to Br^{80} (18 min.). The factor $\frac{\lambda_2}{\lambda_2 - \lambda_1} A_1^0$ is equal to the valve of the intercept obtained when the 4.4 hr. decay curve representing transient equilibrium is extrapolated back to zero time. The values of this intercept for all the experiments reported are given in Table I in the column headed I_2^0. The activities are expressed as counts/min. No correction for the relative counting efficiency of Br^{80} (18 min.) and Br^{80m} (4.4 hr.) was necessary because only the Br^{80} (18 min.) radiation was counted.

In the experiments with liquid bromotrichloromethane and bromobenzene (Table I) the liquid reaction mixtures were prepared for counting by adding to them sufficient organic liquid to fill a counter tube jacket and then extracting the bromine with sodium hydroxide solution. The whole process required less than 30 sec. A time equal to half this measured time was used as the time of separation in the calculations. In the bromobenzene determinations and the third liquid bromotrichloromethane determination (Table I) the organic retention was determined by the growth curve method described above. In the first two liquid bromotrichloromethane determinations (Table I) the decay curve of the Br^{80} (18 min.) in the aqueous extract was determined and extrapolated to the time of separation. The ratio of this intercept to the intercept of the 4.4 hour decay curve obtained from the organic fraction gave the value for the fraction of the isomeric transition events which resulted in bond rupture. The values so obtained are in fair agreement with the one for the same substance obtained by the growth curve method. The latter has the advantage that it does not necessitate density corrections or exact matching of two volumes to be counted.

Bromotrichloromethane.—Michigan Chemical Co. bromotrichloromethane was purified by intense illumination in the presence of inactive bromine. After washing, drying, and fractional distillation, bromine containing Br^{80} (4.4 hr.) was added and the compound was again illuminated to produce CCl_3Br^{80} (4.4 hr.) by photochemical exchange. The elemental bromine was then washed out, the compound was dried and the desired volume was mixed with inactive liquid bromine and allowed to stand for three hours or more before separating and determining the organic yield.

Bromobenzene.—Merck Reagent Grade bromobenzene was irradiated with neutrons in the Argonne National Laboratory CP-3 pile, to produce $C_6H_5Br^{80m}$ (4.4 hr.). It was then washed with aqueous sulfite and with water, and dried. A small center cut from a fractional distillation was used for the experiments reported in Table I. Because of the difficulties introduced by its low vapor pressure no gas phase experiments were done with bromobenzene.

Methyl Bromide.—Eastman Kodak Co. (Pract.) methyl bromide gas was exposed in a vacuum system to solid aluminum bromide containing Br^{80m} (4.4 hr.). CH_3Br^{80m} (4.4 hr.) was formed by the exchange reaction.[11] For the liquid phase runs it was sealed in a 25-cc. tube with 1 cc. of liquid bromine, the mole ratio Br_2/CH_3Br being 27. Tests on the solubility of methyl bromide in bromine indicated that essentially all of that present in these experiments must have been in the solution phase.

The radioactive aluminum bromide was prepared by heating aluminum metal with silver bromide in the vacuum system.

There was no evidence of any aluminum bromide being carried from the exchange chamber with the methyl bromide in any experiment. If any had been so transferred it quite certainly would have exchanged with the large excess of bromine in the reaction mixture, and not have affected the results reported here.

Bromotrifluoromethane.—Bromotrifluoromethane was prepared from fluoroform (obtained from the Minnesota Mining and Manufacturing Co.) and bromine containing Br^{80m} (4.4 hr.), by passing a mixture of the two back and forth over a red hot spiral of platinum wire until the bromine color disappeared. The hydrogen bromide formed in the reaction was removed by passing the product mixture through a sodium hydroxide train. The excess fluoroform was not removed. All operations from synthesis through counting were carried out on a single vacuum train. No liquid phase runs were made with bromotrifluoromethane because it is not sufficiently soluble in liquid bromine.

Results and Discussion

The results of all the determinations made are

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[11] G. B. Kistiakowsky and J. R. Van Wazer, This Journal, **65**, 1829 (1943).

summarized in Table I. Figure 1 shows typical growth curves, one for a sample which yielded an organic retention value of 0.1%, which was indistinguishable from the theoretical curve for 0% retention, and one for a sample which gave 8.8% retention. The latter gave a counting rate of about 1100 c./min. at 2 min. in contrast to 450 c./min. for the former; at 12 min. there was still a 16% difference between the counting rates of the two curves. Calculated values of the organic retention based on the first four individual points of the upper curve were 10.0, 7.7, 9.2 and 8.0%. Corresponding values for the lower curve were 0.7, 1.4, 0 and −1.9. In all of the determinations the experimental points for times longer than 120 min. fell very accurately on a 4.4 hour decay curve and this was plotted with points taken every 20 or 30 min. for at least three hours more.

TABLE I

ORGANIC RETENTION OF Br^{80} (18 MIN.) PRODUCED BY THE ISOMERIC TRANSITION OF Br^{80m} (4.4 HR.) IN ORGANIC BROMIDES, IN THE PRESENCE OF ELEMENTAL BROMINE

Compound	Phase	Reaction mixture, mole % in liq., mm. in gas[a] RBr	Reaction mixture, mole % in liq., mm. in gas[a] Br_2	I_0^2,[b] c./m.	Retention, % Single detns.	Retention, % Average
CCl_3Br	Liquid	0.25	99.75	8460	14.1	
				5450	13.6	
				5000	12.4	13.4
C_6H_5Br	Liquid	.5	99.5	10000	11.6	
				7600	14.4	13.0
CH_3Br	Liquid	3.6	96.4	7000	6.9	
				5400	6.1	6.5
CCl_3Br	Gas	0.4	36	6200	8.8	
				2350	7.8	
				21000	4.8	7.1
CH_3Br	Gas	15	36	9800	5.1	
		6.7	1.8	5100	5.9	
		580	18	4400	5.8	5.6
CF_3Br	Gas	2[c]	51	7140	0.1	
				12000	1.8	1.0

[a] All gas phase experiments were carried out in a 1 liter bulb, except the experiment with methyl bromide at 580 mm. in which a 36-ml. flask was used. [b] I_2^0 is the value of the intercept of the 4.4 hr. decay curve with the zero time axis in plots of the type of Fig. 1. [c] A pressure of about 20 mm. of CF_3H was also present in these reaction mixtures.

The results indicate that: (1) there is partial failure of the carbon-bromine bond to rupture following isomeric transition in all of the cases tested except bromotrifluoromethane; (2) failure of the bond to rupture is influenced by the substituents on the carbon. It is also shown that the organic retention is higher for bromobenzene and bromotrichloromethane dissolved in liquid bromine than it is in the gas phase, but a similar phase change does not affect the retention by CH_3Br.

If part of Br^{80m} (4.4 hr) decayed directly to Se^{80} by positron emission organically bound activity would have been found in our experiments immediately after the separation procedure even though every Br^{80m} which underwent isomeric transition broke the bond (decay by K capture would not be observed with the counting equipment used). This explanation of our results is excluded by the fact that the positron emission[12,13] from Br^{80} has an 18 min. half-life,[12] and by the fact that essentially 100% bond rupture occurs in the case of bromotrifluoromethane (Table I).

The physical evidence that at least one conversion electron is emitted in every isomeric transition event is very good,[2,3,14] and is supported by the chemical evidence of complete bond rupture in bromotrifluoromethane. It must be concluded therefore, that there is a finite probability that bromotrichloromethane, bromobenzene, and methyl bromide molecules, which lose an electron by internal conversion, can undergo both the reorganization which follows loss of such an electron from the K- or L-shell and subsequent charge neutralization without dissociating the carbon–bromine bond.

The number of electrons lost by a bromine atom undergoing isomeric transition varies from one to many.[5,15] It may be that those molecules of a given species in which the carbon–bromine bond fails to rupture are those which have lost only one or only two electrons, whereas those which have lost more always rupture.

The fact that molecules of different compounds show different probability of rupture (*i.e.*, CF_3Br as compared to CCl_3Br and CH_3Br in the gas phase, and CH_3Br as compared to CCl_3Br and C_6H_5Br in bromine solution) is not surprising. The results obtained thus far do not, however, give a clear indication of what variables control this difference. An initial attack on the theory of this type of bond rupture has been made by Magee and Gurnee,[16] but the nature of the problem is too complicated to allow a valid general solution as yet.

The fact that the retention by bromotrichloromethane is higher in solution than in the gas phase may be due to the effect of the solvent cage in favoring primary recombination of the Br^{80} (18 min.) with its parent radical, or may be due to the effect of intermolecular forces on the probability of bond rupture. Either because of the smaller radical or the different intermolecular forces no similar solvent effect is observed with methyl bromide.

Three other examples of partial failure of bond rupture following isomeric transition of Br^{80m} have been reported. They are for the cases of hydrogen bromide (25% failure),[17] deuterium bromide (15% failure),[17] and aqueous bromoplatinate(IV) ion (52% failure).[18] In each of these experiments the conditions were designed to prevent re-entry of the Br^{80} (18 min.) into the parent molecule.

Hamill and Young[8] measured the organic retention of Br^{80} (18 min.) following the isomeric transition of bromine in gaseous CH_3Br^{80m} (4.4 hr.) in the presence of hydrogen bromide. In four determinations they obtained values of 4%, 4%,

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(12) W. C. Barber, *Phys. Rev.*, **72**, 1156 (1947).

(13) J. H. Reynolds, *ibid.*, **79**, 243 (1950).

(14) C. S. Wu, using a high pressure krypton proportional counter, has found that the ratio of the gamma ray peak at 49 kev., corresponding to the first step in the isomeric transition, to that at 37 kev., corresponding to the second step, is less than 0.5%. Private communication.

(15) D. DeVault and W. F. Libby, THIS JOURNAL, **63**, 3216 (1941).

(16) J. L. Magee and E. F. Gurnee, *J. Chem. Phys.*, **20**, 894 (1952).

(17) W. H. Hamill and J. A. Young, *ibid.*, **20**, 888 (1952).

(18) A. W. Adamson and J. M. Grunland, THIS JOURNAL, **73**, 5508 (1951).

1% and a negative value, thus establishing the highest average chemical yield from the isomeric transition observed up to that time. They concluded that their results were consistent with the interpretation that every transition causes bond rupture, just as every transition was known to involve internal conversion. It now appears, from the data of Table I, that the two highest values of the retention in this earlier work were more nearly correct than the lower values.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

The Photolysis of Azoethane[1]

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The photolysis of azoethane was investigated by measurement of the production of nitrogen. The quantum yield was observed to decrease with increasing pressure of azoethane; at the maximum pressure investigated, 1.73 atm., it had fallen to 60% of its low pressure value, which, within the experimental error, can be considered to be unity. The minimum lifetime of activated azoethane was calculated to be 2.5×10^{-11} second, on the assumption of a collision efficiency of unity for deactivation by collision and of a collision diameter of 7 A. for the azoethane molecule. A smaller efficiency for deactivation by collision would correspond to a longer life-time for the excited molecule.

Introduction

The photolysis of azomethane has been studied by many investigators because of its relative simplicity. From the work of Cannon and Rice[3] and others[4] it is known that up to a pressure of 630 mm. the quantum yield at 3660 Å. remains approximately unity. Although some of the excitation energy in photochemical decomposition is initially electronic, it is possible that the mechanism of decomposition involves its transfer to vibrational energy and the eventual accumulation of vibrational energy in a particular bond. If this is the case, collisions should deactivate the molecule and the quantum yield should decrease at sufficiently high pressures. No such decrease has been observed in the case of azomethane at pressures obtainable at room temperature.

Azoethane possesses a larger number of vibrational degrees of freedom than azomethane; one may thus logically expect that an excited azoethane molecule would have a longer life-time than a correspondingly excited azomethane molecule. An investigation of the pressure dependence of the photolysis of azoethane was undertaken for this reason. The data for pressures up to 230 mm. (the vapor pressure at 30°) showed evidence for such a decrease, obscured by the scatter of the measurements. Experiments at still higher pressures, obtained by raising the temperature, confirmed the decrease. Extrapolation from the experimental results indicates that the quantum yield decreases to about 50% of its low pressure value at a pressure of 2 atm., the result being uncertain to an extent of ±10%.

Experimental Part

Preparation of Azoethane.—Diformyl hydrazine[5] was ethylated and subsequently hydrolyzed with hydrochloric acid to diethylhydrazine dihydrochloride. This was oxidized with cupric chloride to the corresponding cuprous chloride azoethane addition product. Azoethane was then prepared by heating the addition compound, a method analogous to that employed by Jahn[6] in preparing azomethane. The azoethane was purified by drying, liquefaction and repeated distillation.

Vapor pressure determinations were performed from −70 to 27° (room temperature). The extrapolated value of the boiling point at atmospheric pressure was found to be 58.3°. The heat and entropy of vaporization at 0° were, respectively, 7,200 cal. deg./mole and 26 cal./mole. Several molecular weight calculations from vapor density measurements gave a mean molecular weight of 87.0 ± 2.0, as compared to expected molecular weight of 86.1.

Optical System.—The same optical system was employed which was used in the photolysis of azomethane.[3] The 3660 Å. line of a medium pressure mercury arc[7] was isolated by the monochromator designed by Cannon and Rice.[8] The lamp was operated at 90–100 volts d.c. Consequently, the monochromatic intensities behind the exit slit (3.97×10^{15} to 1.16×10^{16} quanta per minute) were somewhat smaller than in the previous work. The intensity was measured by a thermopile, which gave a direct reading on a low resistance moving-coil galvanometer of high sensitivity. Corrections for first-order reflections from quartz–gas interfaces and lenses were made for all measurements, as explained below. The correction varied with azoethane pressure; its maximum was 7% of the absorbed intensity.

The absorption coefficient of azoethane was obtained by measuring the transmitted intensity of the 3660 Å. radiation at various pressures. It was found to be 6.82 l.-mole^{-1}-cm.$^{-1}$.

Reaction and Analysis System.—Azoethane was illuminated in a horizontal quartz cell, 9.8 cm. long, with a diameter of 2.5 cm. and windows 1 mm. thick. A chromel heating wire was wound around the cell, which was thermally insulated by means of "Insulag" cement. The temperature of the heated cell was measured by an iron–constantan

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[1] This work was performed with financial aid from the Research Corporation and was presented at the Spring Meeting of the A.C.S., Buffalo, March, 1952.

[2] Department of Chemistry, Polytechnic Institute of Brooklyn.

[3] C. V. Cannon and O. K. Rice, THIS JOURNAL, **59**, 1038 (1937).

[4] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 232.

[5] Either formyl or benzoyl groups can be used to assure symmetrical ethylation. The diformyl hydrazine is more easily prepared and gives better yields.

[6] F. P. Jahn, THIS JOURNAL, **59**, 1761 (1937).

[7] F. Daniels and L. J. Heidt, *ibid.*, **54**, 2381 (1932).

[8] C. V. Cannon and O. K. Rice, *Rev. Sci. Instruments*, **13**, 513 (1942).