

in molecular geometry occurring in response to specific driving forces.<sup>28</sup> The stability of the tropylium ion could furnish the driving force for rearrangement of the  $C_7H_8^{+*}$  ions derived from the various isomers to a complex of a tropylium ion and a hydrogen atom. The corresponding doubly ionized species evidently does not have the same driving force to attain a configuration of such high symmetry.

#### Extension to Other Sets of Isomers

Available data on at least three other sets of isomers—allene, propyne,<sup>20,29,30</sup> and cyclopropene<sup>31</sup>; but-1-yne, but-2-yne, buta-1,2-diene, and buta-1,3-diene<sup>20,29,32,33</sup>; and styrene, cyclooctatetraene,<sup>20,34</sup> and benzocyclobutene<sup>35</sup>—suggest interrelationships similar to those linking the several  $C_7H_8$  isomers. In all three cases, the isomeric spectra are strikingly similar. The spectra of propyne-3- $d_3$ , buta-1,3-diene-1,4- $d_4$ , and five deuterated styrenes show essentially complete loss of positional identity of hydrogen atoms before or during primary decomposition steps. Finally, summing the appearance potential of  $C_3H_3^+$  derived from each  $C_3H_4$  and  $C_4H_6$  molecule in turn and the heat of formation of the molecule gives virtually identical values for the members of each set of isomers. Each such sum is

(28) Compare S. Meyerson and R. W. Vander Haar, *J. Chem. Phys.*, **37**, 2458 (1962).

(29) J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **79**, 5848 (1957).

(30) J. Collin and F. P. Lossing, *ibid.*, **80**, 1568 (1958).

(31) K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *ibid.*, **84**, 3980 (1962).

(32) F. H. Coats and R. C. Anderson, *ibid.*, **79**, 1340 (1957).

(33) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 138.

(34) E. I. Quinn and F. L. Mohler, *J. Research Natl. Bur. Standards*, **62**, 39 (1959).

(35) Unpublished spectrum, this Laboratory. The sample was kindly furnished by F. R. Jensen of the University of California.

the energy of the lowest ionized state of the molecule accessible by electron impact and able to undergo whatever rearrangement and decomposition is required to produce a  $C_3H_3^+$  ion.

If decomposition of such isomers does involve prior rearrangement to a common intermediate at a common energy level, the appearance potentials of the fragment ions can be used to calculate differences in stability of the isomers,<sup>2,3,5</sup> but not bond-dissociation energies in the original molecules. If this view is correct, agreement of bond-dissociation energies derived from appearance potentials with values found by other means<sup>36</sup> must be regarded as fortuitous. A similar conclusion was arrived at earlier from consideration of discrepancies between directly and indirectly measured ionization potentials of free radicals, coupled with labeling evidence of rearrangements in molecule-ions as well as fragment ions.<sup>1,2,37</sup> If a group of isomers all go over into a common intermediate before decomposing, the identities of the decomposition products must reflect the structure of the intermediate rather than that of the original molecule subjected to electron impact. Moreover, no *a priori* reason is apparent for supposing that the structure of such an intermediate is more closely related in any unique fashion to the original structure of one isomer than of another.<sup>37a</sup>

(36) See, for example, R. Schaffer, Ph.D. Thesis, McGill University, Montreal, Can., 1961.

(37) S. Meyerson, P. N. Rylander, E. L. Eliel, and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(37a) NOTE ADDED IN PROOF.—The mass spectrum of a tenth  $C_7H_8$  isomer,  $\Delta^{2,6}$ -bicyclo[3.2.0]heptadiene, and appearance potentials of selected ions in the spectrum, were reported recently [C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, **67**, 1629 (1963)]. This spectrum also resembles closely those of the other isomers. Following the suggestion made previously,<sup>2,3,5</sup> the appearance potential of the  $C_7H_7^+$  ion was used to estimate the heat of formation of the bicyclo[3.2.0]heptadiene as  $2.7 \pm 0.2$  kcal. per mole.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

## Cage Combination and Disproportionation of $CH_3 + C_2H_5 \rightarrow$ Products. The Effect of Solvents and Temperature

BY P. S. DIXON, A. P. STEFANI, AND M. SZWARC

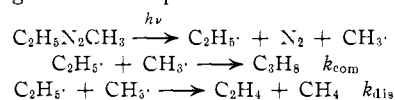
RECEIVED JUNE 12, 1963

The cage interaction of methyl and ethyl radicals was investigated over a wide temperature range ( $-191$  to  $+85^\circ$ ). The radicals were produced by photolysis of  $CH_3N_2C_2H_5$  in isooctane or in glycol. It was shown that the ratio  $k_{dis}/k_{com} = C_2H_4/C_3H_6$  increases with decreasing temperature, the temperature dependence being given by the relation  $k_{dis}/k_{com} \sim T^{-0.85}$  for the isooctane reaction and  $k_{dis}/k_{com} \sim T^{-0.6}$  for the glycol reaction. At all temperatures  $k_{dis}/k_{com}$  is larger for the reaction in glycol than for that in isooctane, although at the lowest temperature,  $-191^\circ$ , their values differ insignificantly. The observed values of  $k_{dis}/k_{com}$  in solution are greater than those reported for the gas phase reaction. The observed features of the reaction  $Me + Et$  resemble those described earlier for the reaction  $Et + Et$ , and it appears therefore that they are characteristic for the interaction of radicals in solution.

In an earlier study of the cage interaction of ethyl radicals,<sup>1</sup> we attempted to determine whether their combination,  $2C_2H_5 \rightarrow C_4H_{10}$ , and disproportionation,  $2C_2H_5 \rightarrow C_2H_4 + C_2H_6$ , involve a common transition state, or whether each reaction proceeds through its own activated complex. Although the results of these investigations did not permit an unambiguous distinction between these two alternatives, they revealed some new features of these processes which are of considerable interest. (1) The ratio  $k_{dis}/k_{com}$  was found to be affected by the solvent, its value being greater for a solution reaction than for the gaseous interaction. Its value seems to increase with the internal pressure of the solvent. (2) A definite temperature dependence of

the ratio  $k_{dis}/k'_{com}$  was observed, disproportionation being favored by lower temperatures in both the gaseous and solution reactions.

It was with the intention of determining whether these phenomena are peculiar to the cage interaction of ethyl radicals or whether they are common to other similar systems that we undertook the present work. The cage interaction of methyl and ethyl radicals produced by photolysis of  $C_2H_5N_2CH_3$  solutions was therefore investigated. The process involves the steps



and hence the value of  $k_{dis}/k_{com}$  is determined by the ratio ethylene/propane.

(1) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551 (1963).

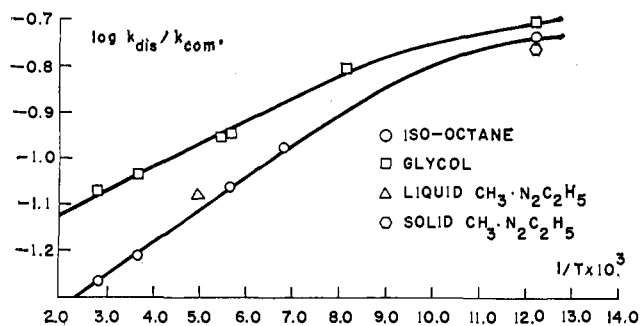


Figure 1.

### Experimental

$\text{CH}_3\text{N}_2\text{C}_2\text{H}_5$  was prepared by oxidizing  $\text{CH}_3\text{NHNHC}_2\text{H}_5$  with mercuric oxide. Although the hydrazine hydrochloride was recrystallized and the azo compound twice fractionated, the final product still contained about 1% of azomethane as revealed by v.p.c. In spite of the presence of this impurity, the prepared product was found to be sufficiently pure for our purpose. The azo compound was stored in a blackened 1-l. flask to avoid its photodecomposition. Before making up each set of samples, the stored gas was condensed in a Dry Ice-isopropyl alcohol bath and degassed to remove any of its decomposition products, or air which might leak into the storing system.

Isooctane and glycol were chosen as solvents since their internal pressures are greatly different. Spectroscopically pure isooctane was freed from traces of olefins by passing through a silica column. Commercially pure glycol was used without further purification and commercially obtained  $\alpha$ -methylstyrene, purified by conventional techniques, was used as scavenger. A high pressure mercury arc (G.E. AH-6) was the source of actinic light. Photolysis was carried out in 10-cc. cylindrical ampoules, each equipped with a constriction to facilitate filling and a breakable capillary tip to permit removal of the contents when the photolysis was completed. The details of filling and removal were described elsewhere.<sup>2</sup>

Ampoules containing 10 cc. of a  $3 \times 10^{-3} M$  solution of the azo compound (mixed with 5 mole % of  $\alpha$ -methylstyrene when a scavenger was required) were immersed in a constant temperature bath and photolyzed for 16 hr. The portion of the ampoules not filled with the liquid were screened with aluminum foil to prevent photolysis of the gaseous azo compound. After completing the reaction, each ampoule in turn was placed in a trap which was then evacuated. The tip was broken and the contents distilled through two traps cooled by a Dry Ice-isopropyl alcohol mixture. The gases were pumped into a mixing chamber where they were thoroughly mixed by a magnetically driven fan, and aliquots were then withdrawn and analyzed by v.p.c. All transfer operations were accomplished by a mercury diffusion pump combined with an automatic Toepler pump.

### Results and Discussion

The experiments were carried out in isooctane and glycol over the temperature range from  $+85$  to  $-191^\circ$  and the results are given in Table I. The scavenger was used only in isooctane at 0 and  $85^\circ$ . At lower temperatures its addition was superfluous as the probability of radicals escaping from the cage was negligible.

The ratio  $\text{CH}_4/\text{C}_2\text{H}_4$  was close to unity for all the experiments carried out at  $T \leq -90^\circ$ . In isooctane and in the presence of 5 mole % of  $\alpha$ -methylstyrene the  $\text{CH}_4/\text{C}_2\text{H}_4$  ratio was unity at  $0^\circ$ , but its value increased to 1.3 at  $+85^\circ$ , showing that at this temperature some methyl radicals react with the solvent. In the absence of scavenger, reaction with the solvent occurred at  $85^\circ$  and at  $0^\circ$ , resulting in a substantial excess of methane over ethylene, and in the formation of a considerable amount of ethane. In all the experiments some ethane was observed. Its formation when bimolecular combination was prevented was due chiefly to the presence of 1% of azomethane in the azo compound.

At 0 and  $85^\circ$  the ratio  $k_{\text{dis}}/k_{\text{com}}$  appeared to be greater in the absence of scavenger than in its presence. It is almost certain that this result is due to the dis-

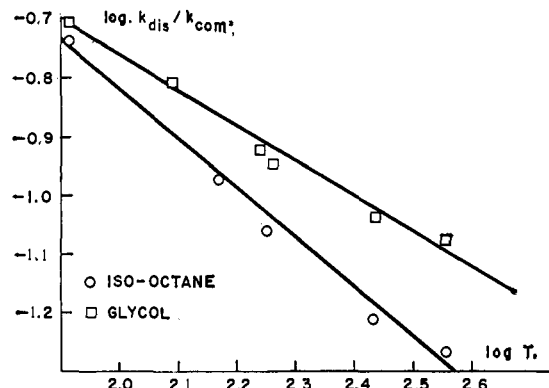


Figure 2.

proportionation reaction  $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$  arising from the bimolecular interaction of two ethyl radicals which diffused out of cage. Such a reaction produces an additional amount of ethylene without forming any propane. The presence of some butane, which is formed under these conditions, provides further evidence confirming the proposed explanation for the apparent increase in the  $k_{\text{dis}}/k_{\text{com}}$  ratio.

TABLE I  
PHOTOLYSIS OF  $\text{C}_2\text{H}_5\text{N}_2\text{CH}_3$  IN SOLUTION

Solvent	Scavenger	No. of expts.	T, °C.	$\text{CH}_4/\text{C}_2\text{H}_4$	$k_{\text{dis}}/k_{\text{com}} = \text{C}_2\text{H}_4/\text{C}_2\text{H}_6$
Isooctane	None	4	-191	1.00	$0.183 \pm 0.006$
Isooctane	None	4	-126	1.07	$.108 \pm .003$
Isooctane	None	3	-95	1.02	$.087 \pm .002$
Isooctane	None	3	0	4.1	$.075 \pm .001$
Isooctane	$\alpha$ -Me-S	3	0	1.00	$.0616 \pm .0006$
Isooctane	None	3	+85	12.6	$.0572 \pm .0010$
Isooctane	$\alpha$ -Me-S	3	+85	1.3	$.0543 \pm .0012$
Glycol	None	3	-191	1.02	$.196 \pm .003$
Glycol	None	3	-150	1.00	$.156 \pm .003$
Glycol	None	3	-99	1.01	$.119 \pm .006$
Glycol	None	3	-90	1.01	$.113 \pm .002$
Glycol	None	3	0	1.23	$.092 \pm .001$
Glycol	None	3	+85	2.24	$.084 \pm .003$
Liquid azo compd.	None	4	-70	1.50	$.084 \pm .001$
Solid azo compd.	None	4	-191	0.97	$.174 \pm .004$

At any particular temperature the ratio  $k_{\text{dis}}/k_{\text{com}}$  was greater in glycol than in isooctane as can be seen from Fig. 1 and 2. The observed values of  $k_{\text{dis}}/k_{\text{com}}$  are higher than the reported ratio of 0.06 for the cross-disproportionation of Me + Et in the gas phase,<sup>3</sup> although at  $85^\circ$  in isooctane the value  $k_{\text{dis}}/k_{\text{com}}$  is, within the experimental errors, identical with that reported for the gas phase.

The ratios,  $k_{\text{dis}}/k_{\text{com}}$ , show a definite temperature dependence, the disproportionation being favored as the temperature was reduced. Plots of  $\log(k_{\text{dis}}/k_{\text{com}})$  against  $1/T$  are linear for  $T > -100^\circ$  (see Fig. 1), their slopes corresponding to the apparent activation energies difference of  $-0.32$  kcal./mole for isooctane and  $-0.23$  kcal./mole for glycol. A peculiar flattening of the curves is observed at the lowest temperatures resembling the shapes of the analogous curve reported for the Et + Et interaction.<sup>1</sup> The plots of  $\log(k_{\text{dis}}/k_{\text{com}})$  vs.  $\log T$  are shown in Fig. 2. They are linear and show no break at the melting temperature of the solvent. (Such breaks were observed in studies of Et + Et interaction.<sup>1</sup>) Their slopes indicate that the ratio

(2) M. Gazith and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 3339 (1957).

(3) J. A. Kerr and A. F. Trotman-Dickenson in "Progress in Reaction Kinetics," Vol. 1, Pergamon Press, London, 1961, p. 107.

$k_{\text{dis}}/k_{\text{com}}$  is proportional to  $T^{-0.85}$  for the reaction in isooctane and to  $T^{-0.6}$  for that in glycol.

The balance of products was again low,<sup>4a</sup> as in the photolysis of azoethane<sup>1</sup> and azomethane,<sup>4b</sup> *e.g.*, we could not account for about 20% of radicals when the reaction proceeded at  $-191^\circ$ . Photolysis of  $\text{CF}_3\text{N}_2\text{CF}_3$  in 2,3-dimethylbutane shows excellent balance of products at  $T \geq -30^\circ$ . At  $-191^\circ$  the ratio  $(\text{BF}_3\text{H} + 2\text{C}_2\text{F}_6)/\text{N}_2$  was again low (about 1.74).

All these observations resemble those reported for the interaction of ethyl radicals,<sup>1</sup> namely (1) the increase in  $k_{\text{dis}}/k_{\text{com}}$  when glycol replaces isooctane as a solvent; (2) the increase of  $k_{\text{dis}}/k_{\text{com}}$  with decreasing temperature which seems to be represented by a function  $T^{-a}$ ; (3) convergence of the  $k_{\text{dis}}/k_{\text{com}}$  values at the lowest temperatures to a limit which seems to be common for all the investigated solvents. It appears,

(4) (a) In reply to the referee's question, we stress that the balance is expected to be low at higher temperatures and in the presence of scavengers, since the reaction of primary radicals with the solvent radicals and the scavenger gives products other than  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{H}_8$ . Such reactions, we believed are unlikely at liquid nitrogen temperature, and therefore the low balance obtained in those experiments puzzles us. (b) R. E. Rebbert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962).

therefore, that these characteristic features of the radical combination and disproportionation are typical of radical interactions in solution.

There is one interesting qualitative difference in the behavior of azoethane and methyl-ethyl azo compound. In the photolysis of solid azoethane the value of  $k_{\text{dis}}/k_{\text{com}}$  was found to be lower than that obtained at the same temperature in other solvents. It was suggested<sup>1</sup> that this result may have been due to the crystal lattice effectively freezing the radical and preserving their initial orientation which favors the combination. In the methyl-ethyl system the  $k_{\text{dis}}/k_{\text{com}}$  ratio was again lower in the solid azo compound than in other solvents, although to a much smaller degree. As this azo compound is not as symmetrical as azoethane, the crystal lattice may have had less influence on the orientation of the radicals and thus combination would not be favored to such an extent.

**Acknowledgment.**—In conclusion, we wish to acknowledge the financial support of this study by the Office of Ordnance through Grant DA-ORD-31-124-61-G72 and by the National Science Foundation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C.]

## The Thermal Decomposition of Cyclobutane at Low Pressures

BY JAMES N. BUTLER AND ROSALIND BARR OGAWA<sup>1</sup>

RECEIVED OCTOBER 15, 1962

The thermal decomposition of cyclobutane has been studied using gas chromatography for analysis at pressures from 43 mm. to  $1.7 \times 10^{-4}$  mm. at a temperature of  $449^\circ$ . Ethylene is the product of a homogeneous first-order decomposition. Propylene and 1-butene are formed in small amounts by zero-order reactions. The shape of the curve of first-order rate constant for ethylene formation as a function of pressure is consistent with the Kassel theory, if  $s$  is taken to be 14, or the Slater theory, if  $n$  is taken to be 16.

### Introduction

The thermal decomposition of cyclobutane in the gas phase has been shown to be a homogeneous unimolecular reaction.<sup>2-5</sup> The primary product is ethylene, although traces of  $\text{C}_3$ ,  $\text{C}_4$ , and  $\text{C}_5$  compounds have been detected.<sup>3,5</sup> The first-order rate constant decreases at low pressures, as predicted by the Kassel or Slater theories<sup>6</sup> of unimolecular reactions, but there has been some disagreement as to the shape of the fall-off curve. Values for the effective number of normal modes contributing to the decomposition have been quoted<sup>5,7,8</sup> which vary from 8 to 20.

### Experimental

The furnace and associated equipment have been described previously.<sup>9</sup> Spherical reactors of 100-ml., 1-l., and 5-l. volumes were made from Pyrex flasks. One thermocouple was used in the small reactor, and four thermocouples in the large reactors. The temperature variation over the surface of the 5-l. reactor was less than  $3^\circ$ , and the drift in temperature during a 2-hr. run was less than  $0.6^\circ$ .

Cyclobutane was prepared by the photolysis of cyclopentanone<sup>10-12</sup> and purified by gas chromatography. The samples used

varied in purity from 99.1 to 99.9%, the principal impurity being a  $\text{C}_5$  compound, probably 2-pentene. The samples contained less than 0.01% of ethylene and less than 0.01% of  $\text{C}_3$  and  $\text{C}_4$  compounds.

Pressures were measured with a wide-bore manometer and cathetometer, or with a McLeod gage. Thermal transpiration corrections were negligible compared to the other experimental errors at pressures above 0.05 mm. At low pressures, corrections based on Liang's equation<sup>13</sup> were used. The parameter  $\phi$  was estimated to be 20 by using Liang's correlation with collision diameter. The largest corrections (at  $2 \times 10^{-4}$  mm.) were 30%.

Samples were expanded into a 300-ml. bulb at room temperature at the conclusion of a run and analyzed by gas chromatography. The composition of the gas was the same within experimental error whether the sampling time was 20 sec. or 10 min. and whether the gas was expanded directly into the bulb or diluted first with approximately 1000 times as much nitrogen and then expanded into the bulb. This eliminates the possibility of a systematic error in the rate constant resulting from the fact that ethylene diffuses through a small opening at low pressures faster than cyclobutane.

Analysis was performed using a Perkin-Elmer Model 154-C vapor fractometer with flame ionization detector. A 150-ft. squalane-coated capillary column maintained at  $0^\circ$  separated all compounds from  $\text{C}_2$  to  $\text{C}_5$  except 1-butene and isobutene. Gas samples were diluted with nitrogen and transferred to a capillary sampling loop with a Toepler pump. Quantitative analysis was made by measuring peak heights. Calibrations would be reproduced to within  $\pm 4\%$ . Between each sample, a blank analysis was performed to see if any residual products remained in the system.

### Results

The principal product of the decomposition of cyclobutane was ethylene. At low pressures small amounts of propylene and 1-butene were also observed. The results obtained near  $449^\circ$  are listed in Table I.

(1) This paper is based on the M.Sc. Thesis of Rosalind Barr Ogawa, Birkbeck College, Malet St., London W. C. 1, England.

(2) C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, **73**, 4497 (1951); F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S.*, **38**, 937 (1952).

(3) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953).

(4) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A218**, 416 (1953).

(5) R. W. Vreeland and D. F. Swinehart, *J. Am. Chem. Soc.*, **85**, 3349 (1963).

(6) N. B. Slater, "The Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

(7) R. E. Powell, *J. Chem. Phys.*, **30**, 724 (1959).

(8) B. S. Rabinovitch and K. W. Michel, *J. Am. Chem. Soc.*, **81**, 5065 (1959).

(9) J. N. Butler, *ibid.*, **84**, 1393 (1962).

(10) S. W. Benson and G. B. Kistiakowsky, *ibid.*, **64**, 80 (1942).

(11) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

(12) R. Srinivasan, *ibid.*, **81**, 1546, 5541 (1959).

(13) S. C. Liang, *J. Phys. Chem.*, **57**, 910 (1953).