

and tertiary hydrocarbons in Fig. 10. These calculations, with no adjustable parameters, reproduce rate constants at all temperatures within about a factor of 2. An activation energy based on the experimental points in Fig. 9 would disagree with the calculated activation energy by several kilocalories, yet the observed rate constants are fairly well predicted by the computations; this point illustrates that wherever possible it is best to evaluate a theory in terms of observed rate constants, not derived quantities such as the Arrhenius parameters,  $A$  and  $E$ .

### Evaluation

Although these calculations seem to have no adjustable parameters, the authors realize that the treatment is partially "adjusted" and do not take the interpretations (constancy of bond order; Pauling's bond-order relation; separability of energy between bonds 1, 2, and 3; activated-complex theory; or separable one-dimensional tunneling factors) at all literally. For fractional H...H bonds one might turn to the well-known hydrogen molecule-ion  $H_2^+$ , or one might take the  $He \cdots He$  cluster as was done here. The first choice gives a poor value for the activation energy of hydrogen molecule reactions, and the second choice gives the good success reported here. The choice of the second model instead of the first is an adjustable concept, if not an adjustable parameter.

Weak points in the numerical aspects of this structure include: rather wide range of values of  $\epsilon$  and  $\sigma$  in

ref. 15, uncertainty in the value and the constancy of Pauling's "constant," and uncertainty in calibrating Sato's triplet function. A strong point in his structure is that results are fairly insensitive to these numerical values; for example, an increase in Pauling's constant increases the activation energy so far as bonding terms are concerned but decreases the contribution of antibonding terms. This method does not calculate the activation energy as the difference in two large total-energy terms. Rather, it calculates directly an energy difference between reactants and the collision complex. This energy difference is further resolved into two more-or-less equal components, the bonding and antibonding terms, with recognition of further nonbonding components.

It is to be expected that further refinements of Lennard-Jones parameters, value of Pauling's constant, and magnitude of the triplet repulsion will destroy some of the remarkable success of these calculations. Thus it is well at this time to claim no more for the method than that it is a very simple technique for predicting rate constants of all hydrogen-transfer reactions based on reactant properties plus something between  $1/2$  and 1 "adjustments."

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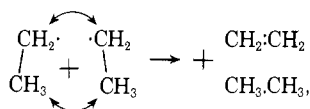
## Combination and Disproportionation of Ethyl Radicals in the Gas, Liquid, and Solid Phases. Some Remarks about the Transition State of these Processes

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

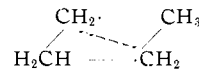
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The combination and disproportionation of ethyl radicals formed by photolysis of azoethane have been investigated in the gas, liquid, and solid phases as well as in a variety of solvents (isooctane, toluene, propanol, glycol, and liquid methane). This study covered a wide temperature range, from  $-191$  to  $+85^\circ$ . It was shown unequivocally that  $k_{dis}/k_{com}$  increases with decreasing temperature both in the gas phase and in solution. This temperature dependence is attributed to terms in  $T^n$ , as it is believed that both processes proceed without any activation energy. The ratio  $k_{dis}/k_{com}$  is larger for solution reactions than for the gas reaction. The largest ratio was found in glycol, the order being glycol > propanol > toluene > isooctane > gas phase. At extremely low temperatures similar values of  $k_{dis}/k_{com}$  were obtained in all solvents. It is not clear, however, whether this observation has a deeper physical significance. It is suggested that the effect of solvent may be due to its internal pressure, and on this basis it was concluded that  $v_{com} \pm v_{dis} \approx 2.4$  cc./mole. The desirability of studies under a few thousand atmospheres of pressure has been stressed. The effect of light of different wave length, scavengers, and concentration has also been examined and it was found that these factors do not affect the ratio  $k_{dis}/k_{com}$ . The models of various transition states for these processes have been examined and fully discussed.

The encounter of two ethyl radicals results in their combination or disproportionation. By labeling the radicals with deuterium it was demonstrated<sup>1,2</sup> that the latter reaction involves a transfer of a hydrogen atom from the  $CH_3$  moiety of one radical to the  $CH_2$  group of the other. This observation was taken as evidence for a head-to-head collision leading to combination and head-to-tail collision resulting in disproportionation.<sup>1,2</sup> However, such a conclusion is not unavoidable, since these experiments show only that the reaction



does not take place. In fact, Bradley<sup>3</sup> and Kerr and Trotman-Dickenson<sup>4</sup> independently suggested that a collision may lead to a common transition state, namely



from which emerge either the products of disproportionation or combination. This idea was further elaborated in a previous paper from this Laboratory<sup>5</sup> where it was proposed that the combination product is formed through the intramolecular dissipation of energy, a process which competes with the intramolecular hydrogen atom transfer giving the disproportionation products.

(3) J. N. Bradley, *J. Chem. Phys.*, **35**, 748 (1961).

(4) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Chemical Kinetics," Vol. 1, Pergamon Press, New York, N. Y., 1961, p. 107.

(5) M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Szwarc, *Proc. Chem. Soc.*, 304 (1962).

(1) M. H. Wijnen and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1092 (1951).

(2) J. R. McNesby, C. M. Drew, and A. S. Gordon, *J. Phys. Chem.*, **59**, 988 (1955).

In solution the radicals may interact either in a bimolecular reaction involving two independently produced radicals which diffused to each other, or through a "cage" reaction<sup>6</sup> in which the encounter takes place between two geminate radicals simultaneously formed in the same location. Since the cage process takes place within  $10^{-10}$  to  $10^{-9}$  sec. after the pair formation, the initial orientation of geminate radicals, which is determined by the structure and conformation of the parent molecule, might be at least partially preserved during their interaction. This in turn should affect the probability of their disproportionation relative to their combination if these two alternative processes arise from different collisions. The hypothesis of two transition states may be checked therefore by determining the ratios  $k_{dis}/k_{com}$  for cage reactions taking place in various solvents and comparing the observed values with those obtained in experiments carried out in the gas phase.

The combination and disproportionation of ethyl radicals in the gas phase was the subject of numerous investigations, the results of the most recent studies being collected in Table I. All the data show that in the temperature range of 50 to 250° the ratio  $k_{dis}/k_{com} = 0.13 \pm 0.02$ ; *i.e.*, its value seems to be constant within the experimental errors. Within the uncertainties of those determinations which we estimated at  $\pm 0.2$  or  $\pm 0.3$  kcal./mole, it was concluded that  $E_{dis} - E_{com} = 0$ .

TABLE I  
DISPROPORTIONATION AND COMBINATION OF ETHYL RADICALS IN  
THE GAS PHASE

System	$\Delta T$ , °C.	$k_{dis}/k_{com}$	Ref.
Phot.; HgEt <sub>2</sub>	75-200	0.36-0.40 (?)	<sup>a</sup>
Phot.; EtCHO	Room temp.	0.1	<sup>b</sup>
Pyro.; HgEt <sub>2</sub>	320-350	.125	<sup>c</sup>
H + C <sub>2</sub> H <sub>4</sub>	Room temp.	.15	<sup>d</sup>
Phot.; EtN <sub>2</sub> Et	Room temp.	.13	<sup>e</sup>
Phot.; EtCOEt	100-250	.12	<sup>f</sup>
Phot.; EtCOEt	25-200	.136	<sup>g</sup>
Phot.; EtN <sub>2</sub> Et	28-150	.12	<sup>h</sup>
H + C <sub>2</sub> H <sub>4</sub>	Room temp.	.14	<sup>i</sup>
H + C <sub>2</sub> H <sub>4</sub>	Room temp.	.1	<sup>j</sup>
Phot.; EtCHO	50-215	.150	<sup>k</sup>
Phot.; EtN <sub>2</sub> Et	-65 to +40	0.16-0.12	This work
Flash phot.; EtN <sub>2</sub> Et	Room temp.	0.117	<sup>l</sup>

<sup>a</sup> K. I. Ivin and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A208**, 25 (1951). <sup>b</sup> F. E. Blacet and J. N. Pitts, *J. Am. Chem. Soc.*, **74**, 3382 (1952). <sup>c</sup> B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, *Proc. Roy. Soc. (London)*, **A218**, 269 (1953). <sup>d</sup> M. J. Smith, P. M. Beatty, J. A. Pinder, and D. J. LeRoy, *Can. J. Chem.*, **31**, 821 (1953). <sup>e</sup> P. Ausloos and E. W. R. Steacie, *Bull. soc. chim. Belges*, **63**, 87 (1954). <sup>f</sup> R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955). <sup>g</sup> D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A244**, 289 (1958). <sup>h</sup> H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958). <sup>i</sup> A. H. Turner and R. J. Cvetanovic, *ibid.*, **37**, 1075 (1959). <sup>j</sup> P. J. Boddy and J. C. Robb, *Proc. Roy. Soc. (London)*, **A249**, 547 (1959). <sup>k</sup> J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1611 (1960). <sup>l</sup> B. C. Roquette and J. H. Futrell, *J. Chem. Phys.*, **37**, 378 (1962).

The cage combination and disproportionation of ethyl radicals was investigated by Smid and Szwarc,<sup>7</sup> who studied the thermal decomposition of propionyl peroxide in isooctane solution in the presence of scavengers such as iodine and benzoquinone. They found the ratio  $k_{dis}/k_{com}$  to be about 0.15 at 65°; *i.e.*, its value was almost indistinguishable from that observed for the gas phase reaction. The studies of the cage decomposition of propionyl peroxide were complicated, however, by some side reactions yielding ethyl propionate and an equimolar mixture of ethylene and propionic

acid.<sup>7</sup> Moreover, it is probable that the primary step of this decomposition produces C<sub>2</sub>H<sub>5</sub>COO radicals, and the ethyl radicals are subsequently formed by their decarboxylation.<sup>8</sup> Thus, the initial separation of geminate ethyl radicals may be relatively large—in fact, considerably larger than the minimum distance required to accommodate the two carbon dioxide molecules formed by the decomposition.<sup>9</sup> Consequently, their initial orientation might be lost at the time of their encounter, and the expected effect of the cage on the ratio of disproportionation to combination could become imperceptible. We investigated, therefore, the cage reaction occurring in the photolysis of azoethane since it is probable that this decomposition directly produces two closely located ethyl radicals initially separated by only one molecule of nitrogen. The original orientation of such radicals, which should favor the head-to-head collision, could be largely preserved during their encounter and this might considerably affect the value of  $k_{dis}/k_{com}$ .

### Experimental

Azoethane, acquired commercially from Merck Co., Montreal, Can., was fractionated and thoroughly deaerated. The gas-chromatographic analysis of the fractionated material showed the absence of impurities. The gas was stored in a blackened 1-l. flask and before withdrawing the aliquots for the photolysis, its contents were frozen and deaerated to remove any trace of air.

Isooctane, toluene, propanol, 2-propanol, and glycol were used as solvents. Spectroscopically pure grade isooctane was freed from traces of olefins by passing through a silica column. The solvent was then distilled through a Todd column. Chemically pure toluene and 2-propanol were fractionated before being used. Commercial, chemically pure glycol was used without any further purifications. The commercial grade styrene, ( $\alpha$ -methylstyrene, and 1,1-diphenylethylene were purified by conventional techniques and used as radical scavengers. Preliminary experiments demonstrated that 3-6 mole % of scavenger was sufficient to suppress any bimolecular reaction of ethyl radicals. At -78° only styrene could be used, since 1,1-diphenylethylene was not sufficiently soluble at this temperature.

In most experiments a high pressure mercury lamp (G.E. AH-6) was used as a source of actinic light. The photolysis was carried out in cylindrical Pyrex ampoules of about 10-cc. volume, each being equipped with a constriction to facilitate filling, and with a breakable capillary tip to permit removal of the contents after completion of the photolysis. All the details of the filling and removal procedures were described elsewhere.<sup>10</sup> In order to find out whether hot radicals participate in the cage reaction, a few experiments were carried out in Vycor ampoules using a low pressure mercury lamp radiating at 2537 Å.

Ampoules containing about 10 cc. of  $3 \times 10^{-3}$  M solution of azoethane in the investigated solvent were mixed with the required scavenger and immersed in a constant temperature bath. The reactants were irradiated for 24 hr. and the parts of the ampoules not filled with the liquid were screened with aluminum foil to prevent any photolysis of the gaseous azoethane. After completion of the reaction, each ampoule was placed in a special trap (see ref. 10) which was then evacuated. The tip of the ampoule was broken by turning the trap, and the contents distilled into a second trap equipped with an internal reflux condenser chilled by a solid carbon dioxide-methanol mixture. Volatile components, *i.e.* nitrogen, ethane, ethylene, and butane, were pumped through the trap fitted with the condenser into a mixing chamber connected to a gas-chromatography analyzer. After thorough mixing of the collected gases by means of a magnetically driven fan, samples were withdrawn for v.p.c. analysis. All the transfers of gases required in the course of these operations were accomplished by a mercury diffusion pump followed by an automatic Toepler pump.

The bulk of the solvent was retained in the trap equipped with the reflux condenser chilled with a solid carbon dioxide-acetone mixture. The reflux was continued for about 45 min. to ascertain that all the butane dissolved in the solvent had been removed. The reliability of this procedure was checked by analyzing prepared mixtures of butane, ethane, and ethylene in isooctane or propanol. A silica chromatographic column was used in the analysis and the gas chromatograms were calibrated with known amounts of the pure components and their mixtures.

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

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(7) J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 3322 (1956).

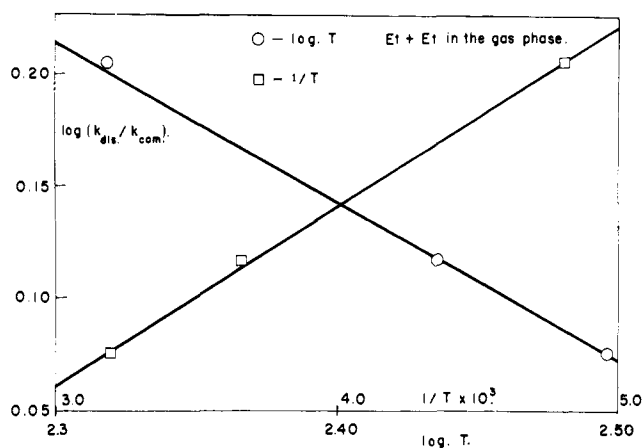


Fig. 1.—Photolysis of azoethane in the gas phase;  $\log(k_{dis}/k_{com})$  plotted vs.  $1/T$  and  $\log T$ , respectively.

The gas phase studies were carried out in 750-cc. Pyrex ampoules, each equipped with a breakseal and a constriction. The partial pressure of the azo compound was kept between 0.2–0.3 mm.; hence no condensation occurred even at  $-78^\circ$ . In most of the experiments a foreign gas ( $\text{CO}_2$  or water vapor) was introduced into the ampoule. The analysis of the products was performed as described above; however, when carbon dioxide was used as a diluent, the contents of the ampoule were first introduced into a trap filled with KOH pellets, the  $\text{CO}_2$  absorbed, and then the remaining gases handled in the usual way. The reliability of this procedure was also checked by analyzing prepared mixtures.

### Results and Discussion

The interaction of ethyl radicals in the gas phase was investigated at  $+40$ ,  $0$ , and  $-65^\circ$ . It was not feasible to extend these studies to lower temperatures because of the low vapor pressure of the azo compound. The pertinent results are collected in Table II. Plots of  $\log(k_{dis}/k_{com})$  vs.  $1/T$  or vs.  $\log T$  gave straight lines corresponding to  $E_{dis} - E_{com} = -0.3$  kcal./mole or the relation  $k_{dis}/k_{com} \sim T^{-0.7}$ .

As the range of  $1/T$  or  $\log T$  investigated by other workers was not so wide as that covered in our study, it was quite possible for them to overlook the minute temperature dependence which we observed. Moreover as we worked at lower temperatures, we were able to avoid the side reactions which become troublesome at higher temperatures and necessitate corrections which might well obscure the small temperature dependence of  $k_{dis}/k_{com}$ .

The values of  $k_{dis}/k_{com}$  reported in this paper fall within the range of the values found by other investigators (see Table I). Also the lack of pressure dependence, observed in other studies, is confirmed by our finding.

TABLE II

#### COMBINATION AND DISPROPORTIONATION OF ETHYL RADICALS IN THE GAS PHASE

Diluent	P, mm.	T, °C.	No. of expt.	$k_{dis}/k_{com}$
$\text{CO}_2$	50	$-65$	5	$0.159 \pm 0.005$
$\text{CO}_2$	700	$-65$	4	$.162 \pm .005$
None	0.2	0	2	$.129 \pm .005$
$\text{CO}_2$	50	0	3	$.131 \pm .005$
$\text{CO}_2$	700	0	3	$.134 \pm .005$
$\text{H}_2\text{O}$	10–50	$+40$	4	$.119 \pm .005$

It is unlikely that  $E_{dis} < E_{com}$  and therefore we prefer to attribute the observed temperature dependence to the factor  $T^{-0.7}$  which apparently appears in the expression for  $k_{dis}/k_{com}$ .

Our most extensive studies of ethyl radical interactions were carried out in isooctane solution. The investigation covered a wide temperature range ( $+85$

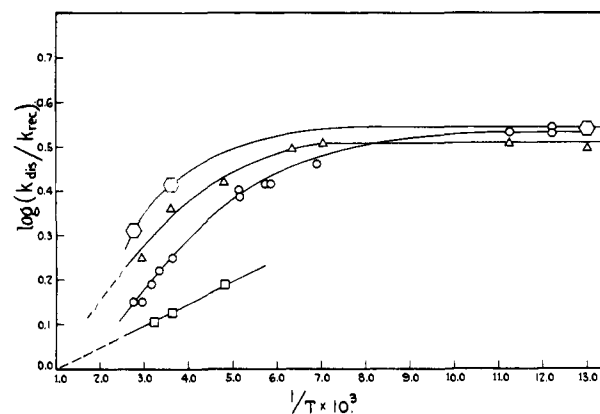


Fig. 2.—Photolysis of azoethane in various solvents:  $\log(k_{dis}/k_{com})$  plotted vs.  $1/T$ ; □, gas phase; ○, isooctane; Δ, propanol-2-propanol; ◊, glycol.

to  $-191^\circ$ ) and all the results are given in Table III. Scavengers were used at  $0^\circ$  and above; at lower temperatures the probability of escape of radicals from the cage was negligible and hence the addition of scavengers was superfluous.

TABLE III

#### PHOTOLYSIS OF AZOETHANE IN ISOOCTANE

Conditions of expt.	No. of expts.	T, °C.	$\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_4/\text{C}_4\text{H}_{10}$
With scavenger	4	85	$1.07 \pm 0.02$	$0.145 \pm 0.007$
None	3	85	$7.09 \pm .08$	$.145 \pm .012$
With scavenger	3	65	$1.07 \pm .02$	$.144 \pm .007$
With scavenger	3	45	$1.06 \pm .02$	$.152 \pm .004$
With scavenger	4	25	$1.05 \pm .01$	$.163 \pm .007$
None	3	25	$3.28 \pm .01$	$.164 \pm .005$
$\lambda = 2537$ ; none	2	25	$5.29 \pm .05$	$.17 \pm .01$
150 atm., none	1	25	3.6	.161
With scavenger	3	0	$1.02 \pm .01$	$.177 \pm .005$
None	5	$-78$	$1.03 \pm .02$	$.246 \pm .005$
None; double azo	2	$-80$	1.06	$.249 \pm .007$
None	3	$-99$	$1.00 \pm .01$	$.260 \pm .005$
None	2	$-128$	$0.96 \pm .01$	$.284 \pm .005$
None	2	$-184$	1.08	.331
None	6	$-191$	$1.01 \pm .01$	$.346 \pm .005$
$\lambda = 2537$ , none	3	$-191$	$1.15 \pm .02$	$.310 \pm .015$

The ratio  $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$  was approximately unity in the experiments carried out below  $-60^\circ$  in the absence of scavengers, or above  $0^\circ$  in the presence of scavengers. The reaction of ethyl radicals with solvent therefore was negligible under these conditions. In the absence of scavenger (see Table III), a substantial excess of  $\text{C}_2\text{H}_6$  was formed at 85 and  $25^\circ$ ; nevertheless, the ratio  $k_{dis}/k_{com} = \text{C}_2\text{H}_4/\text{C}_4\text{H}_{10}$  remained unaltered. In two experiments actinic light of 2537 Å. was used. This led to a definite increase in the  $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$  ratio but hardly affected the ratio  $k_{dis}/k_{com}$ . This type of experiment was particularly significant since the question arose as to what extent the photochemical act leads to local heating which changes the temperature of environment and affects the  $k_{dis}/k_{com}$  ratio. There was no change in  $k_{dis}/k_{com}$  at  $65^\circ$  and we are inclined to ignore the small difference observed in the respective  $k_{dis}/k_{com}$  at  $-191^\circ$ , since the value of 0.310 (see Table III) was calculated from analyses of small amounts of products and may not be too reliable. On this basis it is concluded that the radiative energy is dissipated prior to the interaction of the radicals, and hence the results reflect the proper values of  $k_{dis}/k_{com}$  corresponding to the temperature of the bulk of solution.

The experiments performed with the low pressure mercury lamp ( $\lambda 2537$ ) seem to indicate that a hot radi-

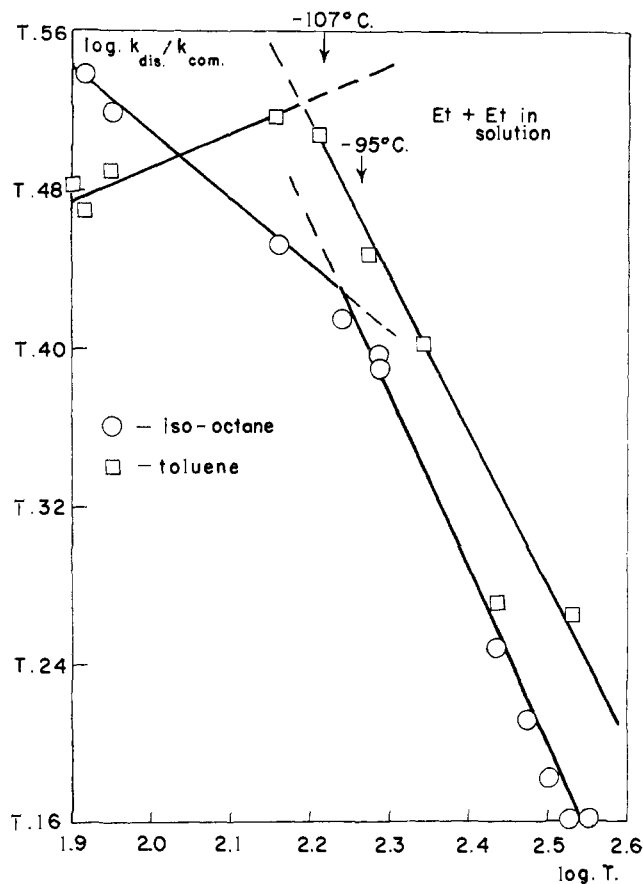


Fig. 3.—Photolysis of azoethane in isooctane and toluene;  $\log(k_{dis}/k_{com})$  vs.  $\log T$ :  $\circ$ , isooctane;  $\square$ , toluene.

cal may abstract a hydrogen from a solvent molecule on its first encounter, while a few collisions with the neighboring molecules occur before the cage interaction of two radicals takes place. This conclusion follows from the observations that under these conditions the ratio  $C_2H_6/C_2H_4$  increased, whereas the ratio  $C_2H_4/C_4H_{10}$  remained unaffected.

In solution the effect of temperature upon the ratio  $k_{dis}/k_{com}$  is much more pronounced than in the gas phase (see Fig. 2). The plot of  $\log(k_{dis}/k_{com})$  vs.  $1/T$ , shown in Fig. 2, is curved and exhibits a peculiar flattening at the lowest temperatures investigated. This graph may be, however, misleading and perhaps a more significant representation of the temperature dependence may be obtained by plotting  $\log(k_{dis}/k_{com})$  vs.  $\log T$ , as shown in Fig. 3. It seems that the results fall on two straight lines which cross at a temperature close to the melting point of the solvent. Apparently  $k_{dis}/k_{com}$  is proportional to  $T^{-0.86}$  in liquid isooctane and to  $T^{-0.33}$  in the solid hydrocarbon—the abrupt change in the temperature dependence reflecting the change of phase. A similar phenomenon was observed for the reaction proceeding in toluene (see Fig. 3).

The results obtained in other solvents are summarized in Table IV and some of them are presented in graphical form in Fig. 2. The effect of solvent upon the ratio  $k_{dis}/k_{com}$  is most striking. From the available data it appears that  $k_{dis}/k_{com}$  in solution is always greater than the respective ratio observed in the gas phase. For example, at  $0^\circ$  the  $k_{dis}/k_{com}$  is 0.130 in the gas phase, 0.177 in isooctane, 0.185 in toluene, 0.202 in 2-propanol, and 0.26–0.27 in glycol. This large increase calls for some comments and may be interpreted in two ways.

It is possible that the  $CH_2$  groups of radicals interact with the solvent and thus become solvated. It would

TABLE IV

Solvent	Scavenger	No. of expts.	T, °C.	$C_2H_6/C_2H_4$	$C_2H_4/C_4H_{10}$
Toluene	None	3	-194	$1.00 \pm 0.01$	$0.304 \pm 0.002$
Toluene	None	2	-191	$0.97 \pm .03$	$.285 \pm .005$
Toluene	None	3	-184	$1.01 \pm .01$	$.309 \pm .002$
Toluene	None	3	-130	$1.08 \pm .03$	$.329 \pm .005$
Toluene	None	2	-110	$1.02 \pm .01$	$.322 \pm .004$
Toluene	None	3	-85	$1.10 \pm .03$	$.287 \pm .003$
Toluene	None	3	-78	$1.33 (?)$	$.271 \pm .003$
Toluene	Styrene	3	0	$1.06 \pm 0.003$	$.189 \pm .002$
Toluene	None	3	0	$4.0 \pm 0.4$	$.184 \pm .003$
Toluene	DPE	3	+65	1.1	$.188 \pm .004$
Toluene	None	3	+65	$5.95 \pm 0.1$	$.167 \pm .003$
Propanols	None	4	-191	$0.97 \pm 0.02$	$.318 \pm .004$
Propanols	None	3	-184	$1.01 \pm .01$	$.325 \pm .002$
Propanols	None	3	-131	1.00	$.324 \pm .003$
1-Propanol	None	2	-116	$0.99 \pm .01$	$.278 \pm .010$
2-Propanol	None	2	-116	$1.11 \pm .04$	$.297 \pm .007$
Propanols	None	3	-115	$1.03 \pm .02$	$.317 \pm .010$
2-Propanol	Styrene	4	-65	$1.02 \pm .01$	$.265 \pm .002$
2-Propanol	Styrene	4	0	$1.05 \pm .01$	$.204 \pm .002$
2-Propanol	Styrene	4	+65	$1.15 \pm .05$	$.178 \pm .001$
Glycol	None	3	-195	$1.06 \pm .03$	$.327 \pm .004$
Glycol	None	3	0	1.3	$.277 \pm .002$
Glycol	None	3	0	$1.4 \pm .1$	$.258 \pm .004$
Glycol	None	3	+85	$1.65 \pm .05$	$.23 \pm .01$
Glycol	None, high concn. of the azo	3	+85	$2.3 \pm .1$	$.203 \pm .004$
Liq. azoethane	None	3	-80	$1.46 \pm 0.01$	0.265
Solid azoethane	None	2	-195	$1.17 \pm .01$	.187
Solid azoethane	None	3	-184	$1.27 \pm .05$	.198
Liquid methane	None	2	-184	$1.00 \pm .02$	$.352 \pm 0.007$

be necessary to desolvate both radical ends to allow their combination, whereas only one end needs to be desolvated to permit their disproportionation. On this basis one expects an increase in the  $k_{dis}/k_{com}$  with increasing solvating power of the solvent. The importance of radical solvation was demonstrated by the recent study of Kassal and Szwarz (*J. Phys. Chem.*, in press), who showed that the heat of solvation of H-atoms in liquid propane is 1.7–2.5 kcal./mole.

Alternatively, one may assume that the volume of activation ( $v^\ddagger$ ) for the transition state of disproportionation is smaller than that of combination. The ratio  $k_{dis}/k_{com}$  would contain therefore a factor  $\exp(-v_{com}^\ddagger - v_{dis}^\ddagger)P/RT$ , where  $P$  denotes the internal pressure of the solvent. Since the internal pressure increases along the series isooctane < toluene < 2-propanol < glycol, this explanation accounts for the observed data. In fact, we may calculate  $v_{com}^\ddagger - v_{dis}^\ddagger$  by using the values of  $k_{dis}/k_{com}$  found at  $0^\circ$  for the gas phase, isooctane, and toluene. From Hildebrand's data it appears that the internal pressure is  $\sim 2900$  atm. in isooctane and  $\sim 3800$  atm. in toluene. Unfortunately no data are available for 2-propanol and glycol. From the equation  $\log\{(k_{dis}/k_{com})_{solvent}/(k_{dis}/k_{com})_{gas\ phase}\} = (v_{com}^\ddagger - v_{dis}^\ddagger)P_{in}/4.617$ , we calculate  $\Delta v^\ddagger = v_{com}^\ddagger - v_{dis}^\ddagger$  to be 2.4 cc./mole based on the results obtained in isooctane and 2.3 cc./mole from those observed in toluene. These are reasonable estimates for  $\Delta v^\ddagger$ .

It should be possible to test these ideas by applying external pressure on the liquid. Unfortunately, our conditions did not permit us to work under pressure higher than 150 atm., and the experiment performed at this pressure (see Table III) shows no change in  $k_{dis}/k_{com}$  as indeed would be expected.

Our results seem to indicate that  $k_{dis}/k_{com}$  approaches approximately a constant value at the lowest temperatures for all the investigated solvents (see Fig. 2). At these temperatures most of the solvents were in a solid or glassy state. We investigated therefore the reaction in liquid methane,<sup>11</sup> which remains fluid even at  $-183^\circ$ .

The results, included in Table IV, show a value of  $k_{dis}/k_{com}$  for this solvent similar to that observed in other media. It is obvious therefore that the constancy of the results obtained in other solvents at  $-191^\circ$  is not due to any trapping of radicals. Moreover, e.s.r. tests show no free spins in the irradiated solutions, implying that the radicals interact under these conditions.

The lack of dependence of  $k_{dis}/k_{com}$  on the nature of the solvent, observed at the lowest temperature, may not be significant, and, in fact, we cannot see any compelling reasons for such behavior of the system. Nevertheless, this observation should not be hastily discarded and deserves further consideration. In fact, recent study of cage interaction of  $CH_3 + C_2H_5$  (P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, in press) showed the same behavior of that system at the lowest temperatures.

An attempt was made to determine how the ratios  $k_{dis}/k_{com}$  differ for radicals which interact before they diffuse out of their place of origin from those which undergo a truly bimolecular encounter in solution. In order to attain a sufficient accuracy in such experiments the photolysis should be performed at a relatively high temperature, to minimize the primary cage recombination, and in a solvent which does not interact with ethyl radicals. It was expected that these conditions would be fulfilled in the cyclic dimer of perfluoropropylene at  $85^\circ$ . It was surprising to find that most of the ethyl radicals which escaped primary interaction formed ethane. The solvent did not contain any residual hydrogen, since photolysis of hexafluoroazomethane in this medium produced a negligible amount of  $CF_3H$ . Apparently  $C_2H_5$  radicals reacted with the azoethane or the butane formed in the process. The extent of this reaction was unusually large since the concentration of azoethane was  $0.016 M$  only. The ratios  $C_4H_{10}/N_2$  and  $C_2H_4/N_2$  were not affected by the addition of scavenger and hence in its presence or absence  $k_{dis}/k_{com} = 0.14$  at  $85^\circ$ .

**Conclusions and the Nature of the Transition State.**—The work described in this paper was initiated for two reasons: (1) to find whether the time of cage reaction is longer or shorter than the period of rotation of an ethyl radical in solution and (2) to accumulate sufficient evidence to allow discrimination between the model involving a common transition state for combination and disproportionation and the alternative one in which each reaction proceeds through its own transition state. We failed, however, to answer unequivocally either question.

Originally, it was expected that in solution the combination should be favored if the time of cage reaction is comparable to the period of rotation. Our findings were not anticipated, and, in fact, they were at variance with our initial ideas. We were forced, therefore, to look for other factors which could affect the course of the reaction. Two alternatives were considered; namely, (1) solvation of the radical ends and (2) the effect caused by the internal pressure of the liquid. The latter interpretation of our results leads to the conclusion that  $v_{com}^\ddagger - v_{dis}^\ddagger \sim 2.4$  cc./mole, and therefore one may anticipate an observable change in

(11) The chemically pure methane was freed from traces of  $C_2H_6$  and  $C_2H_4$  by distilling five times the liquified gas from a trap immersed in liquid oxygen to one immersed in liquid nitrogen. Tests showed the final material to be sufficiently pure for our purpose. The products of photolysis were concentrated by distilling off most of the methane under vacuum at  $-194^\circ$ . The reliability of this procedure was checked by performing analyses of the prepared mixtures.

To dissolve azoethane in methane, the azo compound was evaporated into a 25-l. evacuated flask. The flask was then filled with methane and the mixture condensed in an ampoule chilled with liquid oxygen. This procedure assures a proper mixing of the solute and solvent.

$k_{dis}/k_{com}$  if the reaction would be carried out under pressure of a few thousands of atmospheres.

Our results would be more meaningful if by some other method the time of cage reaction could be compared with the period of rotation of a radical in solution. It is hoped that this will be accomplished by investigating the cage interaction between a  $CH_3$  radical and an allyl radical having one terminal carbon atom labeled by  $C^{14}$ . The most interesting work of Hammond,<sup>12</sup> which is pertinent to this problem, produced ambiguous results owing to the experimental difficulties.

The unusual temperature dependence of  $k_{dis}/k_{com}$  revealed by the present studies need not be interpreted as an indication for  $E_{dis} < E_{com}$ . We believe that neither combination nor disproportionation require any activation energy, and the observed temperature dependence could be attributed to the terms  $T^n$  which might appear in the respective rate constants.

There are other possible explanations of the observed temperature dependence of  $k_{dis}/k_{com}$ . For example, we may again invoke the solvation of radicals and argue that the degree of solvation increases with decreasing temperature. Our observations will be then accounted for by the same reasoning we proposed to explain the solvent effect. However, this explanation will not apply to similar results obtained in the gas phase and, therefore, is not satisfactory. Alternatively, one may argue that the photolysis of azoethane yields  $C_2H_5 + N_2C_2H_5$ , and the fraction of  $N_2C_2H_5$  interacting with  $C_2H_5$  increases with decreasing temperature. Moreover, it would be plausible to assume that  $N_2C_2H_5 + C_2H_5$  gives  $N_2 + C_2H_4 + C_2H_6$  only, and thus  $k_{dis}/k_{com}$  would be greater at lower temperature. The existence of  $N_2 \cdot C_2H_5$  is doubtful, but there is no unequivocal evidence against such a postulate. However, the lifetime of  $N_2 \cdot C_2H_5$  would be expected to be lower if the radicals were formed in a photolysis by  $2537 \text{ \AA}$ . actinic light. This is not the case, as may be seen from the data given in Table III. We doubt, therefore, whether the latter explanation is valid.

The assumption  $E_{dis} = E_{com} = 0$  raises the problem of the validity of the conventional transition state approach in describing the combination and disproportionation of radicals. The conventional transition state is defined by the saddle point of the potential energy hyper-surface. Such a point exists if the *forward* and *backward* reactions require activation energies. However, when one of these processes proceeds without an activation energy, the potential energy hyper-surface exhibits a plateau instead of a saddle point, and consequently the transition state becomes loose. It remains now to decide how "loose" is the transition state of combination and disproportionation—a problem discussed recently by Rice.<sup>13</sup> In his view, the combination of radicals corresponds to an extremely loose transition state—the recombining partners being associated while they rotate freely. Rice even proposed that the loose association of radicals may involve a sort of a hydrogen bond which contributes to their stability.

We may look on this process in a way essentially similar to that outlined by Rice.<sup>13</sup> The trajectories in the phase space which represent two approaching radicals have a width arising from the uncertainty principle. In the region of interaction, the broadening may be sufficiently large to mix the various trajectories and to permit a transition from a trajectory supposedly leading to a head-to-head collision into one corresponding to a head-to-tail collision. Thus, the distinction

(12) S. Wu Ching-Hua, G. S. Hammond, and J. M. Wright, *J. Am. Chem. Soc.*, **82**, 5386 (1960).

(13) O. K. Rice, *J. Phys. Chem.*, **65**, 1588 (1961).

between these two reaction becomes impossible in the interaction region, and one may only inquire what are the probabilities of the emerging system being a pair,  $C_2H_4 + C_2H_6$ , or an energized molecule of butane. Temperature and hydrostatic pressure should affect the probabilities of these events, and hence it is not surprising that these factors influence the value of  $k_{dis}/k_{com}$ . In the gas phase, the pressure is of no importance as long as the reaction is truly bimolecular. In the region of high pressure the process may become termolecular and then the perturbation of the system by the third body is expected to affect the ratio  $k_{dis}/k_{com}$ . At an extremely low pressure the energized molecule of butane may decompose before its excess of energy is removed by collision, and then again the ratio  $k_{dis}/k_{com}$  would be affected.<sup>14</sup>

In solution the perturbing effect of solvent is considerable, the internal pressure being one of its manifestations. We notice that at very low temperatures  $k_{dis}/k_{com}$  is only slightly affected by the nature of solvent, the reaction in solid azoethane being the only striking exception. It is tempting to suggest that the cage formed in the crystal lattice of solid azoethane may have a well-determined shape favoring head-to-head configuration of ethyl radicals. This would lead then to a lower value of  $k_{dis}/k_{com}$  (see Table IV).

The proposed representation of the combination and disproportionation reaction implies that the thermal decomposition of butane, caused by the fission of the central C-C bond, should lead to  $C_2H_4 + C_2H_6$  as well as to two ethyl radicals. To our knowledge the studies of this reaction were never carried out under conditions which would permit an unequivocal answer to this question. The paper by Kupperman and Burton (*Rad. Res.*, **10**, 636 (1959)), quoted by one of the referees, does not provide a clear answer to this problem.

Finally, problems raised by other investigators should be discussed. Bradley<sup>3</sup> points out to the low steric factors which characterize the reactions  $R + HR_1 \rightarrow RH + R_1$  and which contrast the high steric factor of the apparently similar disproportionation reaction. This is not surprising. Both reactions  $R + HR_1 \rightarrow RH + R_1$  and  $R_1 + HR \rightarrow R_1H + R$  require activation energy and therefore one deals here with the conventional transition state requiring a rather rigid configuration of the reagents. The enormous exothermicity of disproportionation makes this process proceed without any activation energy, and this, as was pointed out previously, leads to a loose transition state and therefore to a higher steric factor.

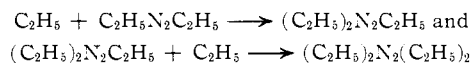
The interesting discussion presented recently by

(14) It seems that this representation of combination and disproportionation resembles that discussed recently by J. N. Bradley and B. S. Rabinovitch, *J. Chem. Phys.*, **36**, 3498 (1962).

Laidler and Wojciechowski<sup>15</sup> is somewhat at variance with our ideas. Laidler considers the disproportionation to be a termolecular reaction at very low pressure; whereas, in our model, the third body is only necessary to stabilize the hot (energized) molecule of butane which results from the encounter of two ethyl radicals. This is unnecessary if the encounter leads to the disproportionation products. Hence, we expect an increase in the ratio  $k_{dis}/k_{com}$  at extremely low pressures, a conclusion that follows also from the model involving two different transition states for combination and disproportionation. It is hoped that the pertinent experiments will be feasible.

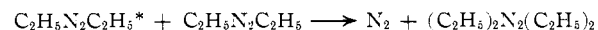
#### Material Balance in the Photolysis of Azoethane.

The experimental results of our studies provide the ratios  $C_2H_4/N_2$ ,  $C_2H_6/N_2$ , and  $C_4H_{10}/N_2$ . It was expected that at low temperature all the radicals formed by the photolysis should be accounted for by these three hydrocarbons, *i.e.*, the ratio  $\{1/2 C_2H_4 + 1/2 C_2H_6 + C_4H_{10}\}/N_2$  should be equal to unity. However, numerous checks showed that even at  $-190^\circ$  this ratio varies between 0.80 and 0.85, although the ratio  $C_2H_6/C_2H_4 = 1$ . One might assume that some of the radicals are lost through formation of hydrazine, *i.e.*



However, the balance appears to be independent of the concentration of the azo compound, and in this respect the results of experiments carried out in liquid azoethane at  $-80^\circ$  did not significantly differ from those obtained in  $10^{-3} M$  solution of azoethane in isooctane.

This puzzling feature of the reaction seems to be confirmed by the results of azomethane photolysis published recently by Rebbert and Ausloos.<sup>16</sup> The cause of this phenomenon is obscure. The only rational explanation which we may offer involves the formation of metastable molecules of excited azoethane, all of which survive until they collide with unexcited molecules of the azo compound and then react according to the equation



Undoubtedly, this feature of the reaction calls for further investigation, since to the best of our knowledge this phenomenon is real and not an artifact of our analytic technique.

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(15) K. J. Laidler and B. W. Wojciechowski, "The Transition State," Special Publication of the Chemical Society, London, No. 16, 1962, p. 46.

(16) R. E. Rebbert and P. Ausloos, *J. Phys. Chem.*, **66**, 2253 (1962).