Studies of Cage Reactions. II. Combination of CH_3 Radicals and of CH_3 and CF_3 into CF_3CH_3

K. Chakravorty, J. M. Pearson, and M. Szwarc

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210.

Received August 25, 1967

Abstract: Cage combination of methyl radicals formed by photolysis of $CH_3N{=}NCH_3$ was investigated in eight solvents at four different temperatures. The probability of combination $p(CH_3) = C_2H_6/N_2$ was accounted for by Noyes' treatment; *i.e.*, $1/p(CH_3)$ is a linear function of $T^{1/2}/\eta$ for each solvent, although slightly different lines were obtained for different solvents. The results led to the conclusion that the probability of combination, α, on each collision is three to five times as high for CH_3 radicals as for CF_3 radicals. This may be accounted for by the higher rate of rotation of CH_3 when compared with CF_3. As in the previous study, $\log P(CH_3) = \log \{(C_2H_6/N_2)/[1 - (C_2H_6/N_2)]\}$ *vs.* $1/T$ is found to be linear, and the lines obtained for all the solvents are again parallel to each other. This constancy of $E_c - E_d$ (the difference of *formal* "activation energies") is striking. Its value is -1.6 ± 0.2 kcal/mole for CH_3 cage combination, whereas for the reaction of CF_3 radicals $E_c - E_d = -2.6 \pm 0.1$ kcal/mole. The mixed cage combination of CH_3 and CF_3 into CH_3CF_3 shows similar features; $p(CH_3,CF_3)$ and $P(CH_3,CF_3)$ are between those found for the homocombinations of CH_3 and of CF_3 and the respective $E_c - E_d = -2.1$ kcal/mole.

The investigation of cage combination reported in the previous paper[1] for trifluoromethyl radicals is extended to combination of methyl radicals to ethane and methyl and trifluoromethyl to CF_3CH_3.

Experimental Section

Methyl radicals were generated by photolysis of azomethane, and photolysis of the mixed azo compound, $CH_3N{=}NCF_3$, was the source of CH_3 and CF_3 radicals. The experimental details of photolytic runs were identical with those given in the previous papers.[1,2] The products were determined by gas chromatography, and from these data we calculated the ratios $C_2H_6/N_2 = p(CH_3)$ and $CF_3CH_3/N_2 = p(CH_3CF_3)$. The bimolecular combination of the primary radicals (CH_3 or CH_3 and CF_3) was prevented by the proper choice of experimental conditions[2] and, if necessary, scavengers were added to the photolyzed systems. No $CF_2{=}CH_2$ was formed in the cage combination of CH_3 and CF_3 radicals. Such a product is observed in their gas-phase combination, and it results from the decomposition of the vibrationally "hot" dimer,[3] *i.e.*, $CF_3CH_3^* \rightarrow CF_2{=}CH_2 + HF$.

Azomethane, acquired commercially, was found to be pure and was used without further refinement. The mixed azo compound was synthesized by condensing trifluoronitrosomethane with methylamine,[4] and the crude product was purified by preparative gas chromatography.

The study was performed in conventionally purified solvents at four different temperatures: 0, 30, 65, and 90°.

Results

The results of our studies of cage combination of methyl radicals are given in Tables I and II. The probability of the combination $p(CH_3) = C_2H_6/N_2$ is given in the former, and the ratios $(C_2H_6/N_2)/[1 - (C_2H_6/N_2)] = P(CH_3)$ are given in the latter. Each figure was obtained by averaging five results of individual experiments. The experimental scatter varied between 5 and 10%.

Similar data were obtained for the mixed combination, and these are summarized in Table III in which the cage combinations of CF_3 and CH_3 radicals are compared.

Table I. Probability of Cage Combination of CH_3 Radicals in Different Solvents

No.	Solvent	$\eta \times 10^3$ at 21°, poise	$p(CH_3) = C_2H_6/N_2$ 0°	30°	65°	90°
3	2,3-Dimethylbutane	3.31	0.68	0.63	0.57	0.51
5	Isooctane	4.84	0.80[a]	0.75[a]	0.69[a]	0.64[a]
2	Toluene	5.75	0.82	0.77	0.71	0.67
7	Chloroform	5.75	0.72	0.66	0.57	0.51
9	Cumene	7.58	0.84	0.79	0.74	0.71
6	Carbon tetrachloride	9.44	0.85	0.81	0.76	
12	Decalin	28.5		0.83	0.77	0.75
14	Benzyl benzoate	89	0.80	0.70	0.67	0.63

[a] These data are taken from ref 2.

Table II. Ratios of Probability of Cage Combination and Diffusion of CH_3 Radicals in Different Solvents

No.	Solvent	$\eta \times 10^3$ at 21°, poise	$(C_2H_6/N_2)/[1 - (C_2H_6/N_2)] = P(CH_3)$ 0°	30°	65°	90°
3	2,3-Dimethylbutane	3.31	2.13	1.72	1.31	1.04
5	Isooctane	4.84	4.2[a]	3.0[a]	2.2[a]	1.8[a]
2	Toluene	5.75	4.41	3.38	2.40	2.03
7	Chloroform	5.75	2.54	1.96	1.34	1.06
9	Cumene	7.58	5.14	3.72	2.81	2.47
6	Carbon tetrachloride	9.44	5.60	4.25	3.11	2.66
12	Decalin	28.5	...	4.75	3.43	3.00
14	Benzyl benzoate	89	4.00 (?)	2.67 (?)	2.02 (?)	1.68 (?)

[a] These data are taken from ref 2.

Discussion

Following the treatment developed by Noyes[5] and outlined in the preceding paper,[1] we plotted $1/p(CH_3)$, or $1/p(CH_3,CF_3)$, *vs.* $T^{1/2}/\eta$. The plots obtained for each solvent were linear (see Figure 1), and the respective intercepts and slopes are given in Table IV. In fact, the points obtained for four solvents (isooctane,

---

(1) O. Dobis, J. M. Pearson, and M. Szwarc, *J. Am. Chem. Soc.*, **90**, 278 (1968).

(2) (a) M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954); (b) A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955); (c) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961); (d) G. E. Owen, Jr., J. M. Pearson, and M. Szwarc, *Trans. Faraday Soc.*, **60**, 564 (1964).

(3) R. D. Giles and E. Whittle, *ibid.*, **61**, 1425 (1965).

(4) A. H. Dinwoodie and R. N. Haszeldine, *J. Chem. Soc.*, 2266 (1965).

(5) R. M. Noyes, "Progress in Chemical Kinetics," Vol. 1, Pergamon Press, New York, N. Y., 1961, p 129.

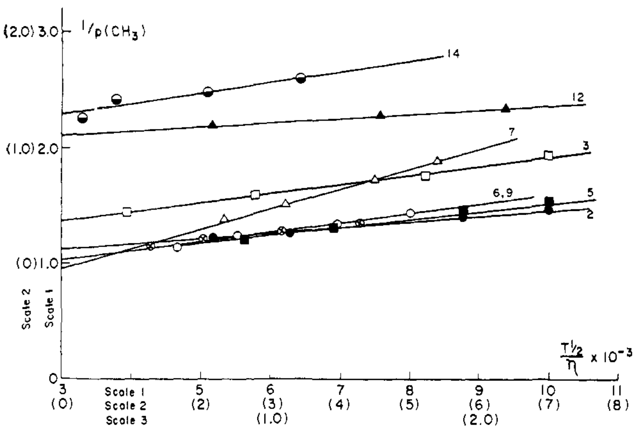

Figure 1. Linear dependence of $1/p(CH_3)$ on $T^{1/2}/\eta$. Scale 1–scale 1: 3; scale 2 (abscissa)–scale 1: 2, 5, 6, 7, 9; scale 3 (abscissa) –scale 2 (ordinate): 12, 14. See Table I for the meaning of the numbers.

toluene, cumene, and carbon tetrachloride) are all virtually on the same line and, with the exception of those obtained for chloroform, all the points fit one flat line as shown in Figure 2.

Table III. Comparison of the Cage Reaction of CH_3 and CF_3 Radicals

No.	Solvent	$P(CF_3)$ (30°)	$P(CH_3)$ (30°)	$-(E_c - E_d)$, kcal/mole CF_3	CH_3
3	2,3-Dimethylbutane	0.49	1.72	2.6 ± 0.1	1.5 ± 0.2
5	Isooctane	0.67	3.0	2.5 ± 0.1	1.8 ± 0.5
2	Toluene	0.73	3.38	2.6 ± 0.2	1.7 ± 0.2
7	Chloroform	0.86	1.96	2.5 ± 0.1	1.8 ± 0.2
9	Cumene	0.90	3.72	2.7 ± 0.1	1.7 ± 0.2
6	Carbon tetrachloride	1.04	4.25	2.7 ± 0.1	1.6 ± 0.2
12	Decalin	2.19	4.75	2.7 ± 0.2	1.8 ± 0.3
14	Benzyl benzoate	1.86	2.67	2.7 ± 0.3	1.8 ± 0.4

Mixed Combination of CH_3 and CF_3 Radicals

No.	Solvent	$P(CF_3,CH_3)$ (30°)	$-(E_c - E_d)_{CF_3,CH_3}$, kcal/mole
3	2,3-Dimethylbutane	1.12	2.1 ± 0.2
5	Isooctane	1.70	2.1 ± 0.2
7	Chloroform	1.40	2.2 ± 0.2
12	Decalin	3.86	2.1 ± 0.3

Table IV. The Slopes and Intercepts of the Linear Relation $1/p(CH_3) = a/2b + (aA/2b\alpha)(T^{1/2}/\eta)$

No.	Solvent	Intercept $= a/2b$	(Slope $= aA/2b\alpha$) $\times 10^3$
	Cage Combination of $CH_3 + CH_3$		
3	2,3-Dimethylbutane	1.4	0.076
5	Isooctane	1.05	0.070
2	Toluene	1.15	0.050
7	Chloroform	0.95	0.16
9	Cumene	1.05	0.077
6	Carbon tetrachloride	1.05	0.077
12	Decalin	1.15	0.090
14	Benzyl benzoate	1.3 (?)	0.25 (?)
	Cage Combination of $CH_3 + CF_3$		
3	2,3-Dimethylbutane	1.0	0.16
5	Isooctane	1.0	0.15
7	Chloroform	0.9	0.24
12	Decalin	1.2	0.19

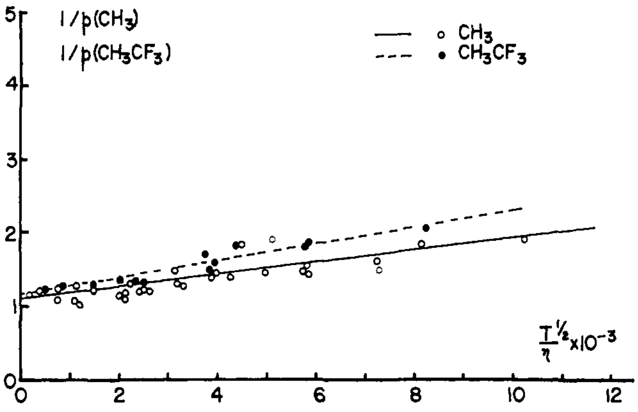

Figure 2. Relation between $1/p(CH_3)$ and $1/p(CH_3,CF_3)$ *vs.* $T^{1/2}/\eta$ for all the experimental points.

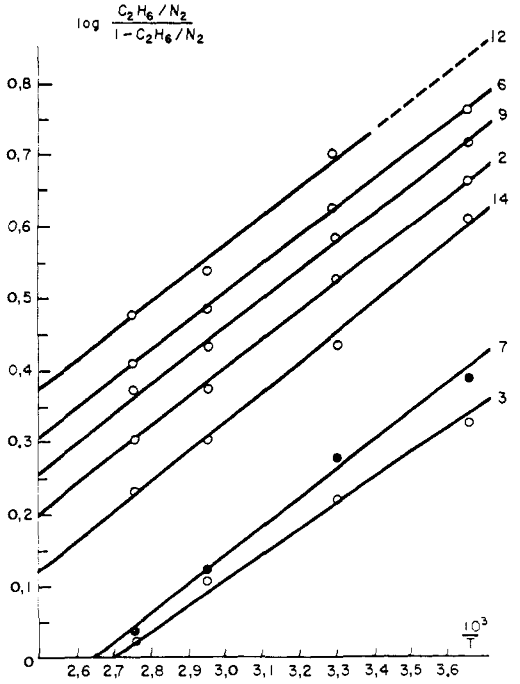

Figure 3. Linear dependence of $\log P(CH_3)$ *vs.* $1/T$. $P(CH_3) = (C_2H_6/N_2)/[1 - (C_2H_6/N_2)]$. See Table I for the meaning of the numbers.

The intercepts of these lines, like most of those found in the previous study, are slightly larger than unity. On the other hand, the slopes of the lines given in Table IV of this paper, when compared with those given in Table III of the preceding one, reveal the striking difference between the CF_3 and CH_3 cage combination. While the values of the former are about 0.07 ± 0.02 (with two exceptions), those of the latter are substantially higher, *viz.*, 0.5 ± 0.2 (with one exception). Accepting the interpretation given in part I and based on the strict adherance to Noyes' model, we conclude that the probability, α, of combination on each collision is greater by a factor of 3 to 5 for CH_3 than for CF_3 radicals. This result may be interpreted as an indication of faster rotation of a CH_3 radical when compared with CF_3. It should be stressed that the translational diffusion constant of CH_3 is expected to be larger than that of CF_3. Hence, on the basis of ordinary translational diffusion the cage combination should be more probable for CF$_3$ than for CH$_3$, contrary to our observations.

The probability of cage combination of CH$_3$ with CF$_3$ seems to be closer to that found for CH$_3$ combination than for CF$_3$ combination. This would be expected if the rate of radical rotation is the determining factor.

It has been suggested by a referee that the different efficiency of the cage combination of CH$_3$ and CF$_3$ radicals may be attributed to different a values; *i.e.*, their initial separation, following the photodissociation, is larger for CF$_3$ than for CH$_3$. It is not obvious, though, why the trend should be in this direction. He also pointed out that a may be an increasing function of temperature. This would lead to a slight curvature in the plots of $1/p$ *vs.* $T^{1/2}/\eta$ making the lines concave. Hence, this suggestion provides an alternative explanation for some low values of intercepts. However, had the temperature been effective in modifying a, a curvature should be observed in individual lines, such as shown in Figure 1 of this paper or Figure 3 of the preceding paper. This is not the case; however, an attempt will be made to extend these studies to a much wider temperature range.

Finally, following the reasons given in part I, we plotted log $P(\mathrm{CH_3})$ *vs.* $1/T$. The results are shown in Figure 3. Again, the resulting lines are parallel to each other; the *formal* activation energies, $E_c - E_d$, are constant within experimental uncertainties, *viz.*, -1.7 ± 0.2 kcal/mole. We feel, therefore, that the constancy of $E_c - E_d$ has some deeper significance which needs further studies. Similar plots for the mixed combination, CH$_3$ + CF$_3$, give $E_c - E_d = -2.1$ kcal/mole, *i.e.*, a value in between those found for CF$_3$ and for CH$_3$ radicals. However, let us stress again that $E_c - E_d$ does not represent conventional activation energies.

Acknowledgment. We gratefully acknowledge the financial support of this study by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society. We also wish to thank the referee for his comments.

Bonding in Donor–Acceptor Complexes. I. Electrostatic Contributions to the Ground-State Properties of Benzene–Halogen Complexes[1a]

Melvin W. Hanna[1b]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received August 14, 1967*

Abstract: The contribution to the energy of formation and the dipole moment of benzene–halogen complexes from the benzene quadrupole–halogen-induced dipole interaction has been evaluated. The results show that this interaction makes an important contribution to these experimental quantities and that it should not be neglected in discussions of the ground state of donor–acceptor complexes. For the benzene–iodine monochloride complex, the quadrupole–dipole interaction was calculated, and it also makes a nonnegligible contribution to the energy of formation. This work suggests that the relative importance of electrostatic and charge-transfer interactions in the ground state of these complexes needs further investigation.

The interactions between "electronegative" and "electropositive" molecules to form donor–acceptor complexes have been an important subject for theoretical and experimental investigation. Much of the work in this field has been summarized in two recent books[2] and numerous reviews.[3–7] The properties of these complexes can be divided into two classes depending on whether they are determined only by the structure of the ground state of the complex or whether they depend on both the ground- and excited-state structures. Properties of the complex such as its geometry, formation constant, enthalpy of formation, dipole moment or change in dipole moment, enhanced intensities and frequency shifts in the infrared spectra, and magnetic properties fall in the first class. The electronic spectrum of the complex falls into the second class.

The charge-transfer model, originally proposed by Mulliken,[8] has been used almost exclusively to rationalize these properties. This model is so well known that only the pertinent points will be summarized here. In the wave function for the ground state of the complex

$$\Psi_N = a\Psi_0 + b\Psi_1 \qquad (1)$$

the "no-bond" wave function Ψ_0 contains all "classical" intermolecular interactions between donor and acceptor

---

(1) (a) Supported in part by Grant GM-09187-04 from the National Institutes of Health, Public Health Service, and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-65; (b) Alfred P. Sloan Fellow.

(2) (a) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 964.

(3) L. J. Andrews, *Chem. Rev.* **54,** 713 (1954).

(4) S. P. McGlynn, *ibid.*, **58,** 1113 (1958).

(5) J. N. Murrell, *Quart Rev.* (London), **15,** 191 (1961).

(6) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13,** 107 (1962).

(7) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3,** 81 (1965).

(8) R. S. Mulliken, *J. Am. Chem. Soc.*, **74,** 811 (1952).