Studies of Cage Reactions. I. The Need for Refined Models. Combination of CF_3 Radicals

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Abstract: The cage combination of CF_3 radicals formed by photolysis of $CF_3N{=}NCF_3$ was investigated at four different temperatures in 14 solvents. The probability of combination, $p(CF_3) = C_2F_6/N_2$, increases with decreasing temperature and increasing viscosity of the solvent. In agreement with Noyes' approach, for each solvent $1/p(CF_3)$ is a linear function of $T^{1/2}/\eta$. Slightly different lines are obtained for different solvents. It seems that some other factor, not considered in Noyes' model, hinders the combination, and its effect becomes more pronounced in less viscous media. Consequently, a plot of $1/p(CF_3)$ *vs.* $T^{1/2}/\eta$ obtained for *all* the investigated solvents and temperatures gives a line which curves up in the regions of low viscosities. The plots of log $P(CF_3)$ *vs.* $1/T$ are also linear. $P(CF_3) = (C_2F_6/N_2)/[1 - (C_2F_6/N_2)] = k_c/k_d$ is the ratio of probabilities of cage combination and of escape from the cage. It is remarkable that the lines obtained for *all* the solvents are parallel, implying that the *formal* "activation energy" difference, $E_c - E_d$, is constant. In contradistinction, the "activation energy" of viscosity increases as the solvent becomes more viscous. The significance of these results is discussed. They seem to indicate that the probability, α, of combination on each collision is small, being between 0.3 and 0.1 for most of the investigated solvents. Various factors which should be included in a more comprehensive model are outlined.

The phenomenon of "cage combination" is well known (see, *e.g.*, ref 1). This effect is observed in systems involving two radicals simultaneously produced in solution at the same location. Two events follow their formation. Either the original partners combine into a dimer, or they diffuse out into the bulk of solution. A suitable experimental setup may then prevent their subsequent combination, and hence in such a system the dimers result from cage reaction only.

Dimers may differ from the parent molecules, decomposition of which produced the radicals. This, *e.g.*, is the case in photolysis of azo compounds and then the probability of cage reaction may be evaluated from the yield of the formed dimer. Thus, the ratio C_2F_6/N_2 determined in the photolysis of hexafluoroazomethane performed under conditions which prevent a bimolecular combination of CF_3 radicals gives the probability of cage combination,[2] denoted by $p(CF_3)$, and $1 - (C_2F_6/N_2)$ is the probability of escape from the cage. The expression $(C_2F_6/N_2)/[1 - (C_2F_6/N_2)]$, denoted by $P(CF_3)$, may be interpreted therefore as the ratio of the formal rate constants of cage combination and of escape.

In the present work such ratios were determined in different solvents and at different temperatures with the intention of investigating how these parameters affect the cage reaction. In this communication we shall deal with combination of CF_3 radicals, and in the following part we shall discuss the combination of CH_3 radicals and the mixed combination of CH_3 and CF_3.

Experimental Section

All the solvents used in this study were purified by conventional distillation methods. Since scavenger techniques were employed to prevent bimolecular combination of nongeminate CF_3 radicals, the presence of small traces of impurities in the solvents was not critical. The radicals which escaped cage combination were rapidly removed by reaction with solvent, *e.g.*, in olefinic or aromatic solvents by addition to a C=C double bond and in many others by hydrogen abstraction which yields CF_3H. Whenever these reactions were slow or impossible, α-methylstyrene, at a concentration not exceeding 5 mole %, was used as scavenger. In this concentration range the scavenger does not interfere with the cage combination, this being verified by the independence of the C_2F_6/N_2 ratios on the α-methylstyrene concentration.

The radicals were produced by photolysis of hexafluoroazomethane using unfiltered light from a high-pressure G.E. AH-6 mercury lamp. Experimental techniques, apparatus, and analytical procedures were described in detail in earlier publications.[3] The cage reaction was investigated at 0, 30, 65, and 90°, and in some solvents also at 120°. The fraction of combined radicals is given by the ratio C_2F_6/N_2 which was determined by gas chromatography. Examples of similar studies are given in ref 4.

Results

The C_2F_6/N_2 ratios were determined by averaging the data of five or more individual experiments. Their scatter was less than 5%, although somewhat greater errors were experienced in benzyl benzoate. The average values of $C_2F_6/N_2 = p(CF_3)$ obtained for 14 solvents at four temperatures are listed in Table I. The viscosity of each liquid at 21° is given in the third column of the table, and for the sake of convenience the solvents are listed in the order of increasing viscosity. Alternatively, the data may be presented as the ratios

$$(C_2F_6/N_2)/[1 - (C_2F_6/N_2)] = P(CF_3)$$

which are listed in Table II. Both ratios, $p(CF_3)$ and $P(CF_3)$, decrease with increasing temperature and also, in most cases, with decreasing viscosity of the solvent. This approximate monotonic relation of $p(CF_3)$ with viscosity of the medium, which could be varied either by changing the solvent or its temperature, is shown in

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[1] R. M. Noyes, "Progress in Chemical Kinetics," Vol. 1, Pergamon Press, Inc., New York, N. Y., 1961, p 129.

[2] L. Herk, M. Feld, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

[3] A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

[4] (a) D. Booth and R. M. Noyes, *ibid.*, **82**, 1868 (1960); (b) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962); (c) R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965); (d) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967).

Table I. Probability of Cage Combination of CF_3 Radicals in Different Solvents

No.	Solvent	$\eta \times 10^3$ at 21°, poise	$p(CF_3) = C_2F_6/N_2$ 0°	30°	65°	90°	120°
8	2-Methylbutane	2.32	0.30	0.21	0.15	0.11	...
3	2,3-Dimethylbutane	3.31	0.42	0.33	0.23	0.19	...
5	Isooctane	4.84	0.49	0.40	0.29	0.24	...
2	Toluene	5.75	0.53	0.42	0.33	0.26	0.22
7	Chloroform	5.75	0.57	0.46	0.36	0.30	...
4	Cyclohexene	6.17	0.51	0.40	0.30	0.25	...
11	Perfluorodimethylcyclobutane	7.33	0.52	0.42	0.30	...	...
9	Cumene	7.58	0.61	0.47	0.38	0.32	...
10	*o*-Xylene	7.85	0.60	0.48	0.39	0.33	...
6	Carbon tetrachloride	9.44	0.64	0.51	0.40	0.34	...
1	Anisole	10.47	0.65	0.55	0.42	0.37	0.29
12	Decalin	28.5	0.77	0.69	0.58	0.50	...
13	Diphenyl ether	38.0	...	0.69	0.59	0.52	0.43
14	Benzyl benzoate	89	...	...	0.53	0.48	0.39

Table II. Ratios of Probability of Cage Combination and Diffusion of CF_3 Radicals in Different Solvents

No.	Solvent	$\eta \times 10^3$ at 21°, poise	$(C_2F_6/N_2)/[1 - (C_2F_6/N_2)] = P(CF_3)$ 0°	30°	65°	90°	120°
8	2-Methylbutane	2.32	0.44	0.27	0.17	0.13	...
3	2,3-Dimethylbutane	3.31	0.74	0.49	0.30	0.24	...
5	Isooctane	4.84	0.96	0.67	0.42	0.31	...
2	Toluene	5.75	1.13	0.73	0.48	0.35	...
7	Chloroform	5.75	1.32	0.86	0.57	0.43	...
4	Cyclohexene	6.17	1.03	0.66	0.44	0.34	...
11	Perfluorodimethylcyclobutane	7.33	1.07	0.72	0.44	...	...
9	Cumene	7.58	1.53	0.90	0.61	0.48	...
10	*o*-Xylene	7.85	1.50	0.94	0.62	0.50	...
6	Carbon tetrachloride	9.44	1.74	1.04	0.68	0.51	...
1	Anisole	10.47	1.87	1.20	0.72	0.59	0.42
12	Decalin	28.5	3.34	2.19	1.36	1.02	...
13	Diphenyl ether	38.0	...	2.22	1.41	1.08	0.75
14	Benzyl benzoate	89	...	...	1.12 (?)	0.94 (?)	0.65 (?)

Figure 1. The plot $1/p(CF_3)$ *vs.* $T^{1/2}/\eta$ accommodates fairly well on a common curve the experimental points obtained for *all* the investigated solvents.

The viscosities of each solvent were determined at a series of temperatures in a capillary viscometer calibrated with liquids of known viscosity. The results are presented in Figure 2 in the form of plots of log η *vs.* $1/T$. These were rigorously linear and from their slopes we calculated the pertinent "activation energies" of viscosity denoted by E_η. The latter and the corresponding A_η are listed in Table IV. Our results compare favorably with those given in American Petroleum Research Project No. 44, Section C. The degree of agreement may be seen from Table V given in the Appendix. However, since solvents of the same quality were used in both the cage reaction studies and in the viscosity measurements, our own viscosity data were used in all the calculations to ensure self-consistency of the reported results.

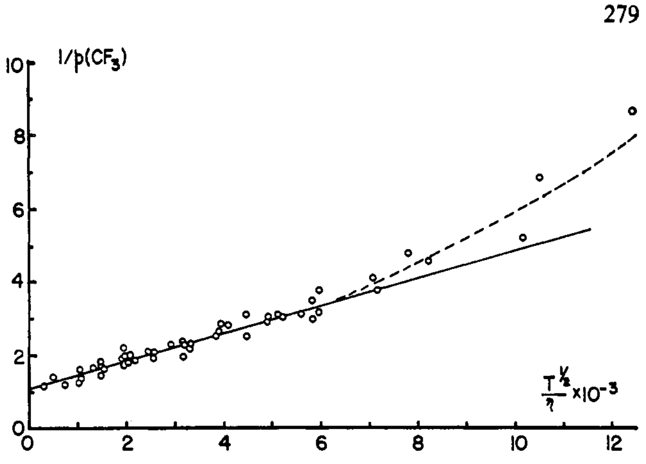

Figure 1. Relation between $1/p(CF_3)$ and $T^{1/2}/\eta$ for all the experimental points.

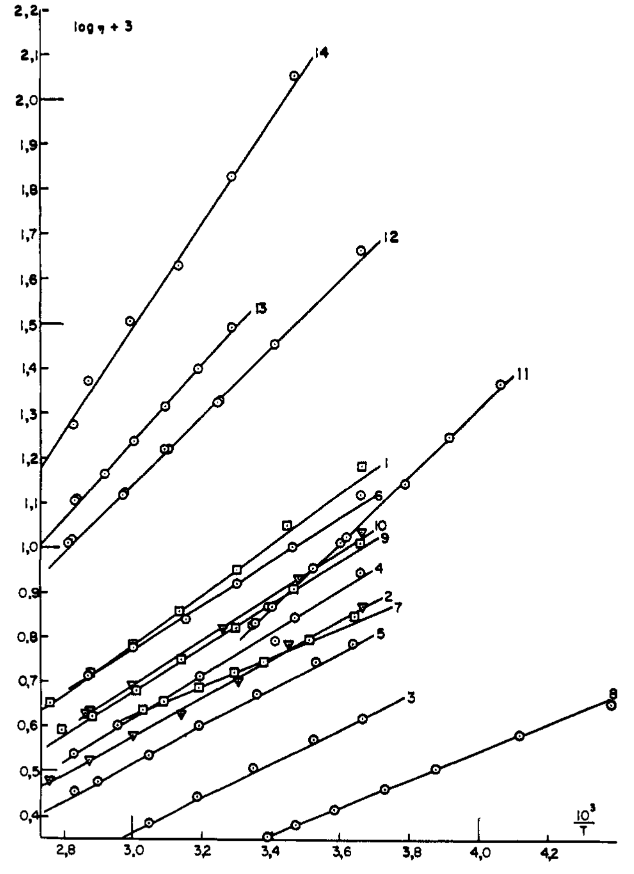

Figure 2. Dependence of log η on $1/T$. Note the more viscous the liquid the higher the "activation energy." See Table I for the meaning of the numbers.

Discussion

The most elegant treatment of the cage reaction was developed by Noyes.[1] In his model the radicals are represented by spheres of radius b, their centers being initially separated by distance a. The reaction takes place in a liquid treated as a continuum characterized by its viscosity η. The diffusion is random, all directions being considered equivalent. The probability of combination on each collision is denoted by α, and after an unsuccessful collision the radicals start again their random walk.

Two questions are posed. (1) What is the probability, β, that the two radicals emerging from an

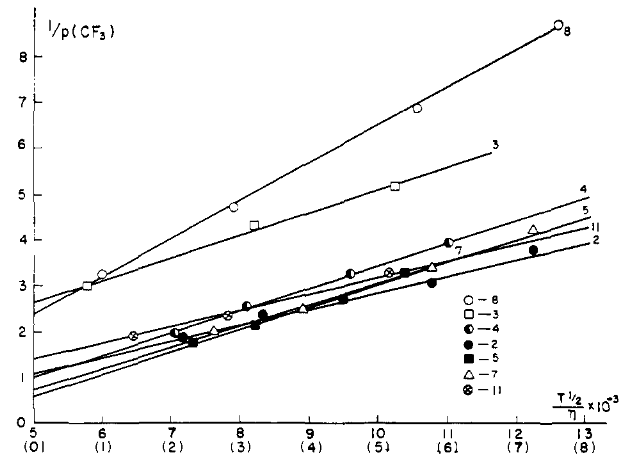

Figure 3a. Linear dependence of $1/p(CF_3)$ on $T^{1/2}/\eta$. Scale 1: 8, 3; scale 2 (abscissa in brackets): 2, 4, 5, 7, 11. See Table I for the meaning of the numbers.

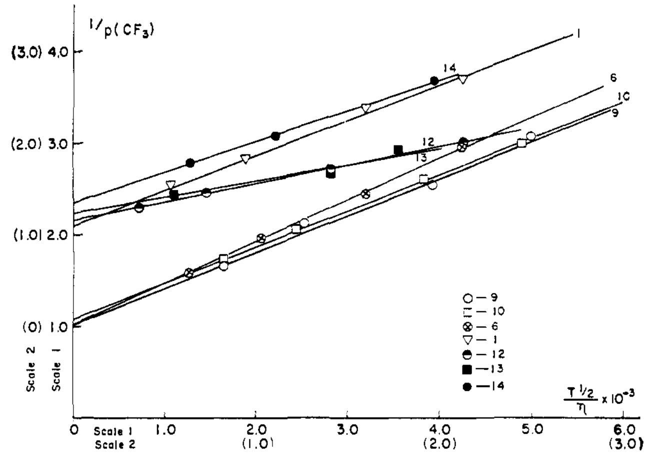

Figure 3b. Linear dependence of $1/p(CF_3)$ on $T^{1/2}/\eta$. Scale 1–scale 1: 6, 9, 10; scale 1–scale 2 (ordinate): 1; scale 2 (abscissa)—scale 2: 12, 13, 14. See Table I for the meaning of the numbers.

unsuccessful collision meet again if their diffusion carries them through an unlimited volume? (2) How much does the probability of the first collision change if the initial distance between their centers is a instead of $2b$?

The calculations led to $\beta = [1 + (mkT/24)^{1/2}/\pi\eta b^2]^{-1}$, and the probability of the first collision was shown to be reduced by a factor of $2b/a$ if the initial separation is a. Hence, the probability, p, of combination of two radicals initially formed at distance a is given by

$$p = (2b/a)\alpha\beta + (2b/a)\alpha\beta^2(1 - \alpha) + (2b/a)\alpha\beta^3(1 - \alpha)^2 + \ldots = (2b/a)\alpha\beta/[1 - \beta(1 - \alpha)]$$

and, therefore

$$1/p = (a/2b\alpha)[(1/\beta) - 1 + \alpha]$$

Substituting $1 + AT^{1/2}/\eta$ for $1/\beta$, where $A = (mk/24)^{1/2}/\pi b^2$, we find

$$1/p = (a/2b) + (a\mathrm{A}/2b\alpha)(T^{1/2}/\eta)$$

i.e., $1/p$ is a linear function of $T^{1/2}/\eta$.

For each solvent the plot of $1/p(CF_3)$ *vs.* $T^{1/2}/\eta$ is linear, and the individual lines are shown in Figures 3a and b. The respective slopes and intercepts are listed in Table III, and its inspection shows, indeed, only minor variations in these parameters, those obtained for the very fluid solvents being exceptional.

Table III. The Slopes and Intercepts of the Linear Relation $1/p(CF_3) = a/2b + (a\mathrm{A}/2b\alpha)(T^{1/2}/\eta)$

No.	Solvent	Intercept = $a/2b$	(Slope = $a\mathrm{A}/2b\alpha$) × 10^3
8	2-Methylbutane	−1.6	0.82
3	2,3-Dimethylbutane	0.1	0.50
5	Isooctane	0.6	0.40
2	Toluene	1.1	0.36
7	Chloroform	0.7	0.30
4	Cyclohexene	1.0	0.48
11	Perfluorodimethylcyclobutane	1.4	0.36
9	Cumene	1.0	0.40
10	*o*-Xylene	1.1	0.40
6	Carbon tetrachloride	1.0	0.45
1	Anisole	1.1	0.38
12	Decalin	1.1	0.40
13	Diphenyl ether	1.25	0.38
14	Benzyl benzoate	1.3 (?)	0.65 (?)

In spite of its approximate nature, Noyes' model accounts satisfactorily for the observed facts. Had viscosity been the only parameter determining the ability of solvent to restrain the radicals and induce their cage combination, all the experimental points would fit one straight line. Although this is not the case, the monotonic relation shown in Figure 1 indicates that the main factors governing the cage phenomenon are properly treated by the theory. The experimental line curves up at regions of low viscosity. Apparently, another factor, independent of viscosity and not included in Noyes' model, is effective in preventing the combination, its role becoming more pronounced as the viscosity of the medium decreases. Tentative suggestions concerned with the nature of such a factor, or factors, are discussed in the last part of this paper. As expected, the deviations from the common line reflect some individual properties of various solvents, which have been omitted in this simplified treatment of cage phenomena. On the other hand, the linear relations shown in Figures 3a and b are most gratifying. Apparently, the model is fair if one wishes to account for the effects of variable viscosity of one medium resulting from changes of temperature.

To what extent do the intercepts and slopes of the lines shown in Figures 3a and b reflect the parameters a, b, and α introduced by Noyes? It appears that the model accounts better for the behavior of viscous solvents than for fluid ones. The unknown parameter, mentioned previously, distorts the lines of low viscosity media and, consequently, the respective intercepts and slopes have then a different meaning than implied by Noyes' model. Indeed, a negative intercept was obtained for 2-methylbutane and too low values were found for two other hydrocarbons. In addition, it remains to be seen whether the relation between $1/p(CF_3)$ and $T^{1/2}/\eta$ would still be linear had the experiments been performed at much lower temperatures.

It is tempting to accept literally the interpretation of slopes and intercepts for the more viscous solvents. Since $A \sim 10^{-5}$, one finds α to be in the range 0.1 to 0.03. Formation of a covalent C–C bond requires some definite orientation of radicals, and therefore not every collision would be effective if the rotation of radicals were hindered during their collision. For example, the high rate of methyl radical combination in the gas phase indicates their free rotation in the transition state. This may not be the case in liquid phase, and then the low values of α become plausible. It should be stressed, however, that this conclusion is based on strict adherence to Noyes' model, which might not be justified.

Our data may be reinterpreted. We may treat the cage process, at least formally, like two competing reactions: the combination characterized by a *formal* rate constant k_c and the escape governed by a *formal* rate constant k_d. Their ratios $k_c/k_d = P(CF_3)$ are listed in Table II. On plotting log $P(CF_3)$ *vs.* $1/T$, as shown in Figure 4, we observed a striking relation. For each solvent a good straight line was obtained, and *all* these lines were found to be parallel to each other. The formal activation energies $E_c - E_d$ (energy of combination minus energy of diffusion) and the respective A factors are listed in Table IV. Its inspection shows that $E_c - E_d$ is virtually constant, its value being -2.6 ± 0.1 kcal/mole in contradistinction to the "activation energy" of viscosity, the absolute value of which increases from 1.4 kcal/mole for a fluid solvent, 2-methylbutane, to 5.6 for the viscous benzyl benzoate. It will be shown in the following paper that the constancy of $E_c - E_d$ is also observed for cage combination of methyl radicals, and we feel, therefore, that this finding has some deeper meaning.

Table IV. "Activation Energies" and A_η[a] for Solvent Viscosities and $(E_c - E_d)$ and the A Factor,[b] for CF_3 Radical Cage Reaction

No.	Solvent	$-E_\eta$, kcal/mole	$A_\eta \times 10^{-2}$	$-(E_c - E_d)$, kcal/mole	$A \times 10^2$
8	2-Methylbutane	1.4	2.2	2.7 ± 0.1	0.4
3	2,3-Dimethylbutane	1.8	1.6	2.6 ± 0.1	0.7
5	Isooctane	1.9	1.8	2.5 ± 0.1	1.0
2	Toluene	2.0	1.9	2.6 ± 0.2	1.0
7	Chloroform	1.5	4.2	2.5 ± 0.1	1.5
4	Cyclohexene	2.1	1.7	2.5 ± 0.1	1.1
11	Perfluorodimethylcyclobutane	3.4	0.2	2.5 ± 0.4	1.1
9	Cumene	2.2	1.8	2.7 ± 0.1	1.2
10	*o*-Xylene	2.2	1.9	2.4 ± 0.1	1.8
6	Carbon tetrachloride	2.3	1.8	2.7 ± 0.1	1.3
1	Anisole	2.7	1.1	2.6 ± 0.1	1.5
12	Decalin	3.6	0.7	2.7 ± 0.2	2.4
13	Diphenyl ether	4.0	0.4	2.8 ± 0.3	2.2
14	Benzyl benzoate	5.6	0.06	2.7 ± 0.3	2.1

[a] Log $\eta = -E_\eta/2.3RT + \log A_\eta$. [b] Log $P(CF_3) = -(E_c - E_d)/2.3RT + \log A$.

Although we are not in a position to suggest a model which quantitatively accounts for all these observations, we wish to point out some features of the system which need further consideration.

(1) The radicals in a "cage" diffuse through a strongly perturbed medium when they tend to combine, whereas their outward movement takes them through an "ordinary" unperturbed liquid. Hence, the diffusion constant should be a function of a. This point was discussed by Noyes,[1] who eventually accepted the assumption of constant $\mathfrak{D}$ as the most reasonable. In fact, the perturbation caused by the photolytic act may substantially increase the free volume of the "cage" region and, therefore, the inward diffusion should require less activation energy than the outward movement.

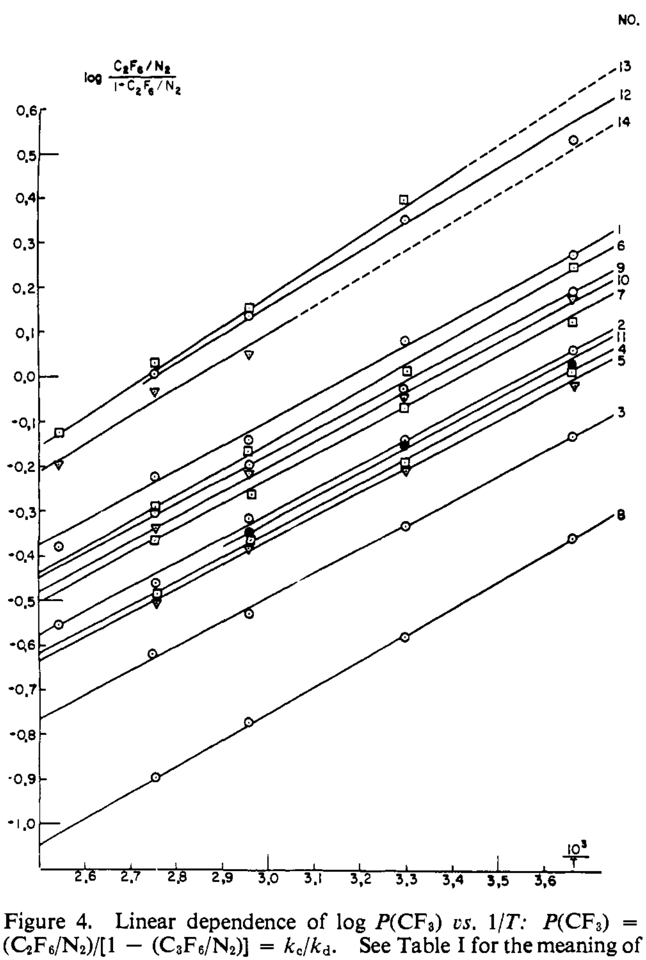

Figure 4. Linear dependence of log $P(CF_3)$ *vs.* $1/T$: $P(CF_3) = (C_2F_6/N_2)/[1 - (C_2F_6/N_2)] = k_c/k_d$. See Table I for the meaning of the numbers.

(2) The solvent was treated as a continuum. However, its molecular structure cannot be neglected when we deal with species having dimensions of molecules. This point is well recognized,[5] and, therefore, deviations reflecting individual properties of different liquids of the same viscosity are not surprising.[6]

(3) The perturbation which increases the disorder and the free volume of the liquid in the "cage" region should lead to relaxation of the system. This is accomplished through a flux of solvent molecules toward the disordered region. Such a diffusion tends to push the radicals together if their initial separation is small in comparison to the dimensions of the solvent molecules, but it tends to part them if this separation is large. Such an effect was invoked by Meadows and Noyes[7] to explain the variations in quantum yield of iodine photolysis at different wavelengths. In their experiments the initial separation of dissociated atoms increased with decreasing wavelength of actinic light, and comparison of the results with theoretical calculations showed a too low quantum yield for long wavelengths and too high for short ones.

In the photolysis of azo compounds, the parting effect of solvent molecules probably prevails. This

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(5) R. M. Noyes, *Z. Elektrochem.*, **64**, 55 (1960).

(6) S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

(7) L. F. Meadows and R. M. Noyes, *ibid.*, **82**, 1872 (1960).

effect is apparently more important for fluid solvents, formed by small molecules which attract each other weakly, than for the viscous ones in which intermolecular forces are large. The flux into the rarefied "cage" region may resemble evaporation and, therefore, it should be enhanced at higher temperatures. Thus, the decrease in the extent of cage reaction would be larger than expected on the basis of radical diffusion only, and this may explain why $|E_c - E_d|$ for some solvents is smaller than E_η (see Table IV).

(4) Finally, the orientation of the radicals necessary for the successful combination may introduce rotational diffusion as a factor determining the cage reaction. This factor is, of course, eliminated in combination of free atoms. Increase in temperature may increase α, the probability of combination on collision, because the rotational diffusion constant increases. This partially cancels the conventional temperature effect of viscosity and may account for the constancy of $E_c - E_d$.

The study reported here was performed with one source of light. However, previous investigations[2] demonstrated that the probability of cage reaction remains unaltered when a low-pressure mercury resonance lamp (λ 2537 Å) was used instead of the high-pressure mercury lamp (λ 3600 Å) and the Pyrex vessels were replaced by Vycor tubes. It appears, therefore, that the excess of energy is rapidly dissipated in this system.

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Appendix

Extensive studies of cage combination of CF_3 radicals at one temperature were completed by Dr. G. E. Owen, Jr. We report his data in Table V together with the viscosities of the respective solvents. The latter are taken from the literature and compare well with those found by us. One may note the approximate monotonic relation of $p(CF_3)$ with η.

Table V

Solvent	$\eta \times 10^3$ at 21°, poise		$C_2F_6/N_2 = p(CF_3)$ at 65°[a]
	Lit. data	Our data	
2-Methylbutene-2	2.1[b]		0.16
3-Methylbutene-1	2.1[b]		0.12
2,3-Dimethylbutane	3.4[b]	3.31	0.23
Tetramethylethylene	3.5[b]		0.20
n-Heptane	4.2[c]		0.25
Hexamethyldisiloxane	4.9[d]		0.27
Isooctane	4.9[b]	4.84	0.28
Toluene	5.8[c]	5.75	0.31
Benzene	6.5[c]		0.28
Cyclohexene	6.6[b]	6.17	0.28
Ethylbenzene	6.7[c]		0.35
Cumene	7.9[c]	7.58	0.39
Tetrachloroethylene	8.9[e]		0.40
Carbon tetrachloride	9.5[e]	9.44	0.38
Cyclohexane	9.7[c]		0.36
Mesitylene	10[f]		0.35
Anisole	10.5[e]	10.47	0.41
1,1-Diphenylethylene	?		0.46
Hexadecene-1	~30[2]		0.46

[a] Data of Dr. G. E. Owen, Jr., from his Ph.D. Thesis, College of Forestry, Syracuse University, 1967. [b] "Physical Constants of the Principal Hydrocarbons," M. P. Doss, Ed., The Texas Co., New York, N. Y., 1942. [c] American Petroleum Institute, Research Project 44, Section C. [d] C. B. Hurd, *J. Am. Chem. Soc.*, **68**, 364 (1946). [e] J. Timmermans, "Physico-Chemical Constants of Pure Organic Substances," Elsevier Publishing Co., New York, N. Y., 1950. [f] J. W. M. Boelhouwer, G. W. Nederbragt, and G. Verberg, *Appl. Sci. Res.*, **2A**, 249 (1950).