In view of possible uncertainties in both the theory and the experiment, the standard deviations in a and b may be considered to be reasonable; and this conclusion can be drawn: The activation energies increase linearly with increasing localization energies.

An interesting fact here is the presence of term b in (E-6) which seems not to have been reported before. A qualitative explanation of b can be obtained by considering a simple but useful model representing potential changes in the addition reaction given by Szwarc[2] and by Binks and Szwarc.[26] The essence of this model is depicted in Fig. 3. Here, r' is a C–H distance at which the potential of hypothetical straight line repulsion becomes equal to the potential of the reactants; δ is the difference between E_{loc} and the potential of hypothetical straight line attraction at r'. Meanings of the other symbols and various assumptions involved in this model are discussed in the original references.[3,26] Simple geometric considerations give these relations

$$a = \left(1 + \frac{\tan \gamma_a}{\tan \gamma_r}\right)^{-1} \qquad \text{(E-7)}$$

and

$$b = a\delta \qquad \text{(E-8)}$$

Binks and Szwarc suggested that, in a series of similar reactions, γ_a and γ_r are approximately constant. If so, r' and the related δ are likely to stay constant also. This would explain why ϵ increases linearly with increasing E_{loc} as shown in (E-6).

Acknowledgments.—We express our appreciation to Dr. F. H. Dickey, Dr. L. O. Morgan and Mr. C. L. Hassel for their valuable discussion and Mr. J. D. Reedy for helping with the experimental work.

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[26] J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY SYRACUSE 10, NEW YORK]

Addition of CF_3 Radicals to Substituted Benzenes

BY I. M. WHITTEMORE, A. P. STEFANI AND M. SZWARC

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The relative rate constants of addition of CF_3 radicals to substituted benzenes have been determined. Electron donating groups such as $-CH_3$ or $-OCH_3$ enhance the reaction, while electron withdrawing groups such as $-CF_3$, -CN, etc., slow it down. Halogenated benzenes are slightly less reactive than benzene, iodobenzene being an exception. The low reactivities of *t*-butylbenzene and *p*-di-*t*-butylbenzene are attributed to shielding of the ortho positions by the bulky *t*-butyl groups. The relative rates of CF_3 radicals addition show poor correlation with Hammett's σ factors. This is anticipated, since each of the measured relative rate constants, k_2, is the sum of the rate constant for all positions, *i.e.*, $k_2 = k_p + 2k_m + 2k_o + k_x$. In spite of this, an unexpectedly good correlation was shown with the ionization potential of the substrate. The relative rate constants of H-atom abstraction have been determined for toluene, mesitylene, ethylbenzene and cumene. These data are compared with those obtained for methyl radicals. It appears that the more reactive CF_3 radicals are more selective. This anomaly calls for further studies. Finally, the effect of solvent upon the cage recombination of CF_3 radicals is discussed.

In an earlier paper[1] we described a technique which allowed us to determine the relative rate constants of CF_3 radical addition to unsaturated and aromatic substrates. The radicals were produced by the photolysis of hexafluoro-azomethane in isoöctane solution, and in the absence of a suitable substrate, all the CF_3 radicals which escaped the cage recombination yielded CF_3H through reaction 1

$$CF_3 + \text{isoöctane} \longrightarrow CF_3H + \text{isoöctyl radical} \quad (1)$$

In the presence of a substrate A, to which radicals may add reaction 2 ensues and the latter competes

$$CF_3 + A \longrightarrow CF_3A\cdot \quad (2)$$

with (1) for CF_3 radicals causing a decrease in the yield of CF_3H as the concentration of A increases. From the magnitude of this decrease the ratio of the rate constants k_2/k_1 was calculated. The details of the experimental technique, the proof of the suggested kinetic scheme and the verification of the equation that gives the k_2/k_1 ratio are reported in ref. 1 and will not be repeated in this paper.

The above method was used recently to determine the k_2/k_1 ratios for a series of non-substituted polynuclear aromatic hydrocarbons,[2] and now it has been applied to a series of substituted benzenes, in order to determine the effect of substituents upon the value of k_2/k_1.

The addition of a radical to substituted benzene may take place in the position *para*, *meta*, or *ortho* to the investigated substituent, and it may also take place on the carbon atom bearing the substituent X. Hence, the measured rate constant k_2 is a sum, *i.e.*

$$k_2 = k_p + 2k_m + 2k_o + k_x$$

where k_p, k_m, k_o, and k_x are the individual rate constants of addition to the respective positions. We hope to develop a technique for determining the various individual rate constants, but at present we can only discuss the changes observed in k_2.

Experimental

The substituted benzenes investigated were: toluene, the xylenes, mesitylene, ethylbenzene, cumene, *t*-butylbenzene, *p*-di-*t*-butylbenzene, fluoro-, chloro-, bromo-, and iodobenzenes, benzonitrile, ethyl benzoate, acetophenone, benzotrifluoride, nitrobenzene, phenol, aniline and anisole. All these compounds, acquired commercially, were purified by conventional techniques before being used.

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[1] A. P. Stefani, L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).

[2] A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3661 (1962).

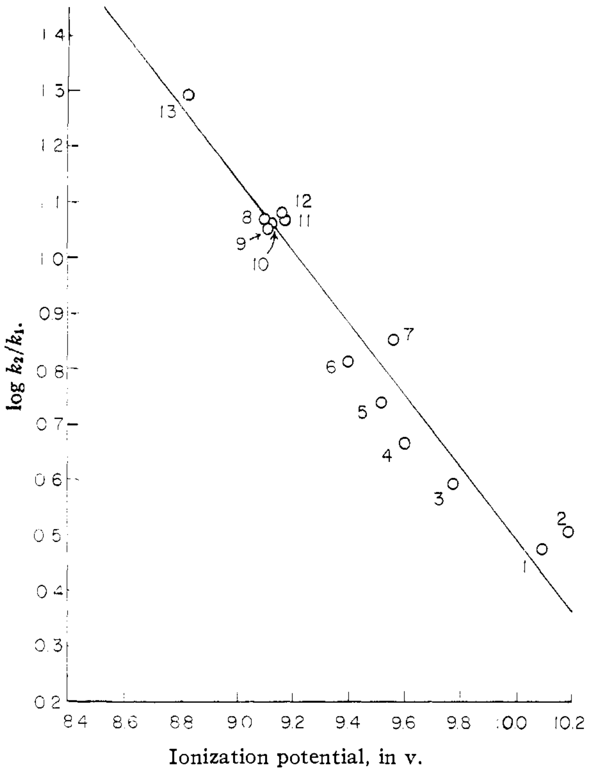

Fig. 1.—Ionization potential *vs.* log k_2/k_1 of substituted benzenes: 1, C_6H_5–CN; 2, C_6H_5–NO_2; 3, C_6H_5–$COCH_3$; 4, C_6H_5–Cl; 5, C_6H_5–Br; 6, C_6H_5–$C(CH_3)_3$; 7, C_6H_5–H; 8, C_6H_5–I; 9, C_6H_5–C_2H_5; 10, C_6H_5–$CH(CH_3)_2$; 11, C_6H_5–CH_3; 12, C_6H_5–OH; 13, C_6H_5–OCH_3.

Spectroscopically pure grade isoöctane was used as a solvent, and this was further purified by passage through a silica column. Hexafluoroazomethane was prepared by the method described by Dacey and Young,[3] and the fractionated gas was stored in a blackened flask. Before being photolyzed, a required sample of the gas was condensed and deaerated thoroughly to remove any trace of nitrogen which could be produced on storage.

The deaerated solution of the reagents, kept in evacuated 10 cc. Pyrex ampoules, was irradiated at 65°, using a water-cooled AH-6 G.E. high pressure mercury lamp as a source of light. The products were analyzed by vapor phase chromatography on a high-vacuum line. A more detailed account of the technique is given in ref. 1.

Results

The results are summarized in Table I. Each of the investigated substrates was studied over the range of concentrations indicated in the second column of Table I, and the constancy of the calculated k_2/k_1's confirmed the validity of the equation used for their calculation. No trend in k_2/k_1 was observed, with the exception of those compounds from which a hydrogen atom may be abstracted. It was shown[1] that in such a case the value of k_2/k_1 computed from the equation

$$(k_2/k_1)_{\text{exp.}} = \{(\text{mole fraction of isoöctane})/(\text{mole fraction of substrate})\}\{(CF_3H/N_2)_{\text{blank}} - (CF_3H)/N_2\}/\{CF_3H/N_2\}$$

is not a constant, but its reciprocal varies linearly with the ratio (mole fraction of substrate)/(mole fraction of isoöctane). The intercept of such a line gives the true value of k_1/k_2, and its slope is equal to k_3/k_2, where k_3 is the rate constant of hydrogen abstraction from the substrate. Such a trend was hardly observed in the methylated benzenes (toluene, the xylenes, and mesitylene), but it was clearly shown in the experiments involving ethylbenzene and cumene.

TABLE I

Relative rate constants of CF_3 addition (k_2) to substituted benzenes: k_1 is the rate constant for the reaction isoöctane + CF_3 → CF_3H + isoöctyl radical. All the data obtained at 65°; concentration of the azo compound 5 × 10^{-3} mole/l.

Substrate	Concn. range, mole %	Expts.	k_2/k_1
Benzene	1.0–10	5	7.1 ± 0.3
Toluene	2.5–15	16	11.7 ± 0.6
o-Xylene	3 –15	5	13.5 ± 0.3
m-Xylene	1.6– 9	5	20.5 ± 1.3
p-Xylene	8 –20	4	17.2 ± 0.7
Mesitylene	0.8– 4.3	8	41.2 ± 1.4
Ethylbenzene	4 –20	4	11.3 (extrp. to 0%)
Cumene	3 –15	4	11.4 (extrp. to 0%)
t-Butylbenzene	3 –15	4	6.5 ± 0.1
p-Di-*t*-butylbenzene	5 –33	5	3.8 ± .3
Fluorobenzene	15 –35	7	3.4 ± .2
Chlorobenzene	2.5–12	4	4.6 ± .1
Bromobenzene	2 –20	5	5.5 ± .1
Iodobenzene	10 –25	4	11.7 ± .4
Benzotrifluoride	3 –33	5	2.1 ± .2
Benzonitrile	9 –55	4	3.0 ± .3
Nitrobenzene	15 –40	4	3.2 ± .6
Ethyl benzoate	6 –40	5	7.9 ± .5
Anisole	4.5–30	5	19.8 ± .9
Phenol	2.0–10	5	11.8 ± .6
Acetophenone	5 –20	5	4.3 ± .8
Aniline	1 – 7	3	45.3 ± .8

It is obvious that the above described method of determining k_3/k_2 is experimentally not too reliable, since errors in determining the slope of a line are much greater than those of individual measurements. Hence, an alternative method for determining k_3/k_2 was developed. Photolysis of hexafluoroazomethane was studied in the pure substrate, and the amounts of N_2, CF_3H, and C_2F_6 produced in the reaction were determined. Assuming that $\{2 - (CF_3H + 2C_2F_6)/N_2\}$ represents the CF_3 radicals which add to the substrate, while CF_3H/N_2 corresponds to those that abstract from it a hydrogen atom, the ratio k_3/k_2 is calculated to be

$$k_3/k_2 = (CF_3H/N_2)/\{2-(CF_3H + 2C_2F_6)/N_2\}$$

The relevant data are collected in Table II.

The latter method is justified by the previous observations[1] which showed that the ratio $(CF_3H + 2C_2F_6)/N_2 = 2$ if the photolysis is carried out in isoöctane, *i.e.*, in a medium in which the addition reaction does not take place. Moreover, the fact that the ratio CF_3H/N_2 is independent of the time of photolysis and the initial concentration of the azo compound (see Table II) proves that CF_3H is not formed by reactions involving the products or intermediates (adduct radicals) of the photolysis. This observation is not surprising, since the maximum of substrate's conversion in any experiment was less than 0.5%, and in some experiments even less than 0.1%. Our conclusions are also supported

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(3) J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).

TABLE II

k_3' is the rate constant of H abstraction per active H.

Time photolys., hr.	$[CF_3N_2CF_3]$ (mole/l. × 10^3)	CF_3H/N_2	C_2F_6/N_2	k_3/k_2	k_3'/k_1
Toluene (k_2/k_1 = 11.7)					
16	8.8	0.039	0.32	0.030	0.12
16	8.8	.029	.32	.022	.09
33	8.8	.038	.34	.029	.11
$18^{1/2}$	5.6	.039	.30	.029	.11
$18^{1/2}$	15.7	.045	.30	.033	.13
$18^{1/2}$	25.0	.050	.30	.037	.14
				Av.	0.12 ± 0.02
Ethylbenzene (k_2/k_1 = 11.3)					
16	8.8	0.16	0.35	0.14	0.80
16	8.8	.16	.35	.14	.79
33	8.8	.17	.37	.16	.90
17	8.4	.165	.355	.15	.83
17	29.5	.16	.36	.14	.82
				Av.	0.83 ± 0.05
Cumene (k_2/k_1 = 11.4)					
16	8.8	0.27	0.38	0.275	3.14
16	8.8	.24	.37	.24	2.75
33	8.8	.265	.39	.28	3.15
17	17.2	.25	.38	.25	2.85
17	37.4	.245	.41	.26	2.98
				Av.	2.98 ± 0.18
Mesitylene (k_2/k_1 = 41.2)					
$18^{1/2}$	5.6	0.040	0.32	0.030	0.13
$18^{1/2}$	15.5	.038	.365	.031	.14
$18^{1/2}$	24.6	.040	.36	.032	.14
				Av.	0.14 ± 0.01

by the observations reported by Charles and Whittle[4] and Charles, Pearson and Whittle,[5] who found that for pressures of benzene vapor lower than 10 mm., all the secondary radicals formed in the process reacted again with CF_3 giving either a di-substituted adduct or CF_3H. However, at benzene pressures higher than 40 mm., all the CF_3 radicals reacted with benzene, which competed efficiently with CF_3-secondary radical reactions. The concentration of aromatic substrates in liquid is about 3000 higher than that in the gas phase at 40 mm., and hence no CF_3-secondary radical reaction could be expected in our system. Further indication showing that our assumptions are right comes from comparison of k_3'/k_1 for toluene and mesitylene (see Table II). For both compounds, essentially identical values were obtained for k_3'/k_1, as had been expected, in spite of the fact that the addition to mesitylene is about 3.5 times faster than the addition to toluene.

In some photolysis experiments carried out in the aromatic hydrocarbons a faint pink color developed. This color deepened on exposure of the solution to air. Apparently, the cyclohexadienyl radicals interacted with the undecomposed hexafluoroazomethane and produced some colored azo-compounds. No attempt was made to investigate further this reaction which apparently did not interfere with the processes studied in the course of this work.

Discussion

The results presented here demonstrate that CF_3 radicals add readily to benzene and its derivatives. Such an addition reaction was observed by Charles and Whittle[4] and by Charles, Pearson and Whittle,[5] who studied the interaction of benzene, toluene and *o*-xylene with CF_3 radicals in the gaseous phase. They concluded from their observations that the primary product of the reaction is a substituted cyclohexadienyl radical which eventually dimerizes or disproportionates. The formation of such adduct radicals was postulated earlier for the reaction of benzene with methyl radicals,[6] and recently DeTar and Long[7] succeeded in isolating and characterizing the dimers of such radicals formed by the reaction of benzene with phenyl radicals.

The kinetics of photolysis, studied in the course of our work, prove that under our experimental conditions the CF_3 radicals did not interact with the secondary radicals or products of the reaction. The simplicity of the reacting system was achieved by keeping the stationary concentration of radicals at a sufficiently low level and by limiting the extent of the reaction to a very low conversion. This is demonstrated by the independence of the k_2/k_1 ratio of the mole fraction of the substrate, and of the concentration of the azo-compound (see Table III).

TABLE III

EFFECT OF $CF_3 \cdot NN \cdot CF_3$ CONCENTRATION ON THE RATE CONSTANT (k_2) OF ADDITION OF CF_3 RADICALS TO BENZENE.[a] SOLVENT, ISO-OCTANE; T = 65°

$[CF_3N_2CF_3]$, mole/l. × 10^4	Moles of isoöctane / Moles of benzene	CF_3H/N_2	k_2/k_1
2.94	6.38	0.155	7.6
5.33	6.38	.154	7.6
9.65	6.38	.156	7.5
21.5	6.38	.159	7.2
30.2	6.38	.158	7.3

[a] These data were obtained by Mr. H. Komazawa of this Laboratory.

The substituents markedly affect the rate constant of the over-all addition (k_2), aniline being about 6 times as reactive as benzene while the reactivity of benzotrifluoride is lower by a factor of 3 (see Table I). On the whole, electron donating groups such as methyl or methoxy increase the reactivity while electron withdrawing groups such as $-CF_3$, $-NO_2$, $-F$, or $-Cl$ reduce it. This behavior is to be expected for an electrophilic radical such as CF_3,[8] and a more complete discussion of this topic was presented in previous papers from this Laboratory.[1,2] The addition of methyl or phenyl radicals to substituted benzenes,[9,10] or naph-

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[4] S. W. Charles and E. Whittle, *Trans. Faraday Soc.*, **56**, 794 (1960).

[5] S. W. Charles, J. T. Pearson and E. Whittle, *ibid.*, **57**, 1356 (1961).

[6] (a) M. Levy, M. Steinberg and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 3439 (1954). (b) M. Levy and M. Szwarc, *ibid.*, **77**, 1949 (1955).

[7] D. F. DeTar and R. A. J. Long, *ibid.*, **80**, 4742 (1958).

[8] (a) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950). (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y., 1957.

[9] W. J. Heilman, A. Rembaum and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

[10] D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

thalenes,[11] showed an opposite behavior. These reactions were hindered by electron donating groups, such as $-OCH_3$ or $-N(CH_3)_2$,[9,11] and enhanced by electron withdrawing groups. These observations seem to justify the classification of methyl and phenyl radicals as slightly nucleophilic reagents.

The correlation of the rate constants of addition of CF_3 radicals (k_2) with Hammett's σ is rather poor. This is not unexpected as Hammett's relation refers to reactions taking place in the position *para* or *meta* to the substituent, while k_2 represents a sum $k_p + 2k_m + 2k_o + k_x$ as was remarked earlier. The work of Hey and his co-workers[10] showed that the addition of phenyl radicals in the position ortho to the substituent is favored. In addition, we have reason to believe that CF_3 radicals may also add to the carbon atoms bearing the substituent, although such a reaction is not expected to be favored. Hence, the contribution of $2k_o + k_x$ to k_2, which probably is not negligible, vitiates Hammett's type of relation although the general trend in reactivities indicating, as expected, a negative ρ value remained unaltered.

A closer inspection of Table I substantiates the conclusion about the centers of the addition. The rate constants of CF_3 radical addition to toluene, ethylbenzene and cumene are essentially identical, whereas a substantially lower rate constant was observed in the reaction of *t*-butylbenzene. A similar observation was made by Hey, *et al.*,[12] who noticed a low rate of addition of phenyl radicals to *t*-butylbenzene and attributed this result to steric shielding of the ortho positions by the *t*-butyl group. Our observation indicates, therefore, a high probability of CF_3 radical addition to the ortho positions, since the shielding effect of a *t*-butyl group is further substantiated by the extremely low reactivity of *p*-di-*t*-butylbenzene. It is tempting to suggest that the relatively low reactivity of *o*-xylene, when compared with the *para* and *meta*-isomer, may be again due to the blocking of one of the *ortho* positions.

The rate of addition of the strongly electrophilic CF_3 radicals should be facilitated by the low ionization potential of the substrate. Such a relation was reported previously[1]—the log k_2 was found to be linear with the ionization potential for the series ethylene, propylene, butene-1 and iso-butene. The point of addition seems to be fixed for that series, the reaction taking place on the $=CH_2$ group. On the other hand, as remarked in the preceding sections, there are several different centers of the addition for substituted benzenes, and therefore it is surprising that a relatively good linear relation is observed for the relevant log k_2's and the respective ionization potentials. This relation is shown in Fig. 1, the ionization potentials being taken from a recent paper by Crable and Kearns[13] and the monograph by Field and Franklin.[14]

The increase in reactivity along the series fluorobenzene, chlorobenzene, bromobenzene and iodobenzene is parallel to that observed in similar reactions of methyl[9,11] and phenyl radicals.[10] This suggests that the increase in reactivity should be attributed to resonance and not to the inductive effect. The k_2 value for iodobenzene may be too high since photolysis of iodobenzene could produce a trace of iodine which would react with CF_3 radicals. Moreover, it is probable that a fraction of the CF_3 radicals did not add to iodobenzene but abstracted iodine atoms, producing $CF_3I + Ph\cdot$. The extent of this reaction is not known, since no attempt was made to isolate CF_3I in the products. However, studies of the halogen abstraction reaction by CF_3 radicals are contemplated.

The results listed in Table II deserve some comment. The last column of this table gives the relative rate constants of the H abstraction reaction per reactive hydrogen atom. In Table IV these results are compared to those obtained for methyl radicals, the latter data being taken from a paper by Meyer, Stannett and Szwarc.[15] It is remarkable to find that the more reactive CF_3 radical appears to be more selective for these abstraction processes. Such a result cannot be explained by the formation of an intermediate, *e.g.*, a π-complex, since the considerably more basic mesitylene does not appear to be much more reactive in respect to H abstraction than toluene (see Table II). We suggest tentatively that these observations might reflect a different degree of participation of polar forms $R^+\ldots H\ldots CF_3^-$ to the transition state of the abstraction reaction—(see, *e.g.*, the discussion of Cl atom reactions in Walling's monograph Free Radicals in Solution). However, further studies are necessary to account for such a large effect as is observed. Unfortunately, the presently available data for the respective abstractions from aliphatic hydrocarbons by CF_3 radicals[16] are not sufficiently precise to draw any final conclusions on this subject. We plan, therefore, to investigate this matter further.

TABLE IV

The relative rate constant k_3' of H abstraction reaction per reactive hydrogen: T, 65°, toluene being considered as the standard.

Hydrocarbon	Type of C-H	Relative k_3' for CF_3	Relative k_3' for CH_3
Toluene	Primary	(1)	(1)
Mesitylene	Primary	1.17	0.94
Ethylbenzene	Secondary	6.9	4.14
Cumene	Tertiary	24.8	12.9

In a recent paper by Holmes and Kutschke,[17] published after this manuscript was completed, the k_3/k_2 value for toluene in the gas phase was

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[11] J. Gresser, J. H. Binks and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 5004 (1959).

[12] J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 794 (1954).

[13] G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

[14] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

[15] J. A. Meyer, V. Stannett and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 25 (1961).

[16] (a) G. O. Pritchard, H. O. Pritchard, H. I. Schiff and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **52**, 849 (1956). (b) P. B. Ayscough, J. C. Polanyi and E. W. R. Steacie, *Can. J. Chem.*, **33**, 743 (1955). (c) P. B. Ayscough and E. W. R. Steacie, *ibid.*, **34**, 103 (1956). (d) R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1465 (1957). (e) G. O. Pritchard, H. O. Pritchard and A. F. Trotman-Dickenson, *Chem. and Ind.* (London), 564 (1955).

[17] J. L. Holmes and K. O. Kutschke, *Trans. Faraday Soc.*, **58**, 333 (1962).

reported to be 0.056 at 65°. This value compares reasonably with that found in the course of this work, *i.e.*, 0.03, which was carried out in the liquid phase. We have some reservation about Holmes and Kutschke's results, which are discussed elsewhere.[18] It seems that these workers did not eliminate the reaction $CF_3(CH_3)\cdot C_6H_5\cdot + CF_3 \rightarrow CF_3(CH_3)\cdot C_6H_4 + CF_3H$. Participation of this step in their reaction might account for their high value of k_3'/k_2.

(18) P. S. Dixon and M. Szwarc, *Trans. Faraday Soc.*, in press.

NOTE ADDED IN PROOF.—The reaction of CF_3 radicals with toluene performed in the gas phase at 65° showed that $CF_3H/N_2 = 0.071$ leading to $k_3/k_2 = 0.037 \pm 0.003$, in agreement with our liquid phase results. In these experiments the concentration of hexafluoroazomethane was varied by a factor of 5 without affecting the CF_3H/N_2 ratio. Only minute amounts of C_2F_6 (less than 0.5%) were observed in the products.

In conclusion, we wish to acknowledge the financial support of this investigation by the National Science Foundation Grant G-19044.

[CONTRIBUTION FROM THE INSTITUTE FOR MUSCLE RESEARCH AT THE MARINE BIOLOGICAL LABORATORY, WOODS HOLE, MASSACHUSETTS]

Solvent Effects in Radical Ion Formation[1]

BY IRVIN ISENBERG AND SPENCER L. BAIRD, JR.

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Electron spin resonance techniques indicate that the interaction of tetramethyl-*p*-phenylenediamine and chloranil will lead to the formation of Wurster's blue and chloranil free radicals in polar solvents but not in non-polar solvents. Presumably, this occurs through the dissociation of a charge transfer complex. Similar results are obtained for the interaction of diethylaniline and chloranil.

Introduction

Mulliken[2] pointed out that solvent effects should alter the nature of donor–acceptor interaction. In general, one may expect polar solvents to increase the amount of charge transferred.[3] In the present note it will be shown, in a rather direct fashion, that changing from a non-polar solvent to a more polar solvent can be accompanied by a change from complex formation in which there is little or no dissociation to form free radicals, to one in which there is appreciable free radical formation.

The complexes studied were tetramethyl-*p*-phenylenediamine/chloranil and diethylaniline/chloranil. Solvent polarity was altered by using various mixtures of chloroform, 1,2-dichloroethane and ethanol.

The use of the tetramethyl-*p*-phenylenediamine/chloranil system has a number of advantages. The charge transfer complex has been previously studied.[4] The free radical ions of each partner have been investigated by spin resonance methods[5–7] and consequently can be identified easily. Furthermore, another rather unexpected advantage, to be described below, also occurs.

Technique.—Optical spectra were run on a Cary Model 14 Spectrophotometer. Electrin spin resonance spectra were run on a Varian Model V-4500 Spectrometer modified to run as a double modulation instrument.[8] A flat quartz specimen chamber of internal dimensions approximately 0.3 mm. × 5 mm. × 25 mm. was used for all spin resonance studies.

N,N,N^1,N^1-Tetramethyl-*p*-phenylenediamine dihydrochloride (Eastman) was dissolved in water, neutralized with KOH and extracted with ether. The ether was pumped away. The residue was redissolved in ether, dried with $MgSO_4$, filtered and dried by pumping. The powder was melted in a molecular still and distilled onto a cold finger. The white crystalline solid thus obtained was kept at approximately −40° until used.

Chloranil (Matheson, Coleman and Bell) was recrystallized twice from acetone.

Ethanol, 1,2-dichloroethane and chloroform were redistilled before use.

Diethylaniline was distilled twice in a Hickman still. After the second distillation it was pale yellow, almost colorless.

Experimental Procedure and Results

A flow system using a four jet nylon mixing chamber and nitrogen pressure was used to mix 10^{-2} *M* chloranil in chloroform and 10^{-2} *M* tetramethyl-*p*-phenylenediamine in ethanol in equal amounts and flow the mixture into the electron spin resonance sample tube. This yielded a signal showing a superposition of the chloranil free radical and the Wurster's blue free radical (Fig. 1). The time for the liquid to flow from the mixing chamber into the flat portion of the sample tube could be varied from about 1 sec. to about 10 sec. without any observable change in the signal. When the flow was stopped the chloranil free radical gradually diminished, dropping about 15% per minute while the Wurster's blue free radical concentration did not change.[9] This rather striking constancy was observed a number of times and permitted a simplification of technique.

Since the Wurster's blue concentration did not change, the effect of the solvent could be observed without the use of a mixing chamber. The tetramethyl-*p*-phenylenediamine and chloranil solutions could thereafter be mixed by hand. The sample chamber could then be filled and a spectrum taken. By observing the hyperfine components on the far wings of the Wurster's blue free radical where they were

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(9) After about an hour there appears to be a perceptible diminution in the Wurster's blue concentration.