

ion. In these latter cases it has been suggested that the increases in the moments may possibly arise from compression of the CoCl₄⁻² ion by the large cations in the crystal, thus causing distortions in the symmetry of the ligand field.²⁴ While it cannot be argued that this may not be the case, it appears that still another effect may be equally responsible for the observed increases in μ_{eff} values of the diazonium salt complexes. Infrared spectral studies are consistent in showing that aside from the primary charge transfer (*i.e.*, the initial process in which an electron is transferred from the C₈H₁₀N₃ radical to the MCl_n fragment to form the ion pair, [C₈H₁₀N₃]⁺[MCl_n]⁻) there is a secondary partial charge transfer from the filled orbitals of the chloride ligands to a vacant π -orbital on the diazonium cation.^{5,25} Such a process would conceivably account for distortions in the symmetry of the ligand field about any of the metal ions in question. Pryce²⁶ has shown that axial distortions in the symmetrical fields of Fe(III) and Mn(II) ions involve energy having an order of magnitude such that would increase the spin orbital contribution to the temperature-dependent paramagnetic susceptibility by an order of magnitude of 10⁻⁵ e.m.u./g.-ion. At room temperature, this would correspond to a maximum increase in μ_{eff} of about 10⁻¹ B.M. It is curious to see that the order of magnitude by which μ_{eff} is increased due to an axial distortion is in agreement with what is observed here.

It is also established that charge transfer complexes not having a large covalent stabilization of the dative-bond structure have a triplet level lying very close to the ground state.¹⁴ It is not uncommon to find that such complexes exhibit paramagnetism resulting from the thermal population of the well stabilized triplet level. This, for example, has been found in charge transfer complexes of *p*-phenylenediamine with *p*-benzoquinones.²⁷ Thus it is equally possible that magnetic effects reported here may result also from the thermal

(25) L. J. Theriot, H. B. Jonassen, E. A. Boudreaux and M. Ayres, to be published.

(26) M. H. L. Pryce, *Nuovo Cimento Suppl.*, **6**, 817 (1957).

population of the low-lying triplet level in the diazonium cation of these complexes.

In view of this and the other data previously mentioned, it is our contention that in complexes of *p*-dimethylaminobenzediazonium chloride containing FeCl₄⁻, MnCl₄⁻², CoCl₄⁻² and CuCl₆⁻⁴ ions the observed increases in μ_{eff} (Table IV) above the μ_{eff} values for analogous ions in CsCl lattices (Table III) are to some extent due to a charge transfer process leading to axial distortions in the ligand field about the metal ions. Such distortion should account for an increase in the spin-orbit coupling contribution to the magnetic moment. Alternately, it is suggested further that thermal population of a low-lying triplet level in the complex may also account for the observed results. Although it is not feasible to attempt any rigorous derivation for demonstrating this, the well known phenomena of orbital spreading and charge delocalization inherent in charge transfer processes could conceivably apply here.

It is not to be denied that other physical processes, including compression of the anions by the cations in the crystal, could lead to a similar effect of increasing the magnetic moment; however, it is felt that in view of this, the anisotropy data, electronic spectral data (appearing in part II) and infrared spectral studies^{5,25} indicate that a charge-transfer interaction seems also to be of importance. Other effects may also be involved, but it would be exceedingly difficult at this time to make a quantitative estimate of the various contributing factors. Furthermore, it is not intended that this account be taken as more than qualitative support for charge transfer based on the observed effects.

Acknowledgments.—We wish to express our gratitude to the National Science Foundation for supporting this work. We are also grateful to Prof. S. P. McGlynn of Louisiana State University, Baton Rouge, La., for helpful discussions, and to Prof. F. A. Cotton of M.I.T. for his criticisms regarding part of this work.

(27) H. Kainer, D. Biji and A. C. Rose-Innes, *Naturwissenschaften*, **41**, 303 (1954).

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Studies of Irreversibility of CF₃ Addition. Reactions with Some *cis* and *trans* Isomers and the Problem of *cis*-*trans* Isomerization

BY H. KOMAZAWA, A. P. STEFANI AND M. SZWARC

RECEIVED MARCH 16, 1963

Kinetic evidence presented here proves that the addition of CF₃ radicals to a variety of substrates is irreversible at 65° whether the reaction proceeds in solution or in the gas phase. At 150° in the gas phase a small fraction of CF₃-benzene adduct seems to decompose into CF₃ + benzene. No decomposition was observed for the CF₃-CHCl:CHCl adduct radicals. On the other hand, it was shown that under the same conditions, photolysis of 4 mole % of CF₃N₂CF₃ in 99% *trans*-dichloroethylene may lead to complete isomerization of the ethylene. Further studies indicated that the isomerization is caused by Cl atoms produced through the reactions: CF₃ + CHCl=CHCl → CF₃CHClCHCl· and ·CHClCH(CF₃)Cl → CHCl=CHCF₃ + Cl; *i.e.*, the dissociation of the adduct radical into Cl + CHCl=CHCF₃ takes place while under the same conditions no fission of the ·CHCl-CHCl-CF₃ bond is observed. The dissociation of vibrationally excited radicals is reviewed and the difference between the rupture of a C-R bond (R = polyatomic moiety) and a C-X bond (X = an atom) is considered. Gradation in reactivities of some substrates toward CF₃ addition is discussed.

The relative rate constants of CF₃ addition to various substrates such as olefins, aromatic hydrocarbons, acetylenes, etc., were determined by a technique described in earlier papers.¹⁻⁴ The radicals were produced by photolysis of hexafluoroazomethane, and their

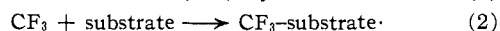
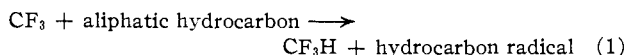
(1) A. P. Stefani, L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).

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

(3) I. Whittemore, A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3799 (1962).

(4) P. S. Dixon and M. Szwarc, *Trans. Faraday Soc.*, **59**, 112 (1963).

addition to the investigated substrate proceeded simultaneously with the hydrogen abstraction from an aliphatic hydrocarbon used as a solvent (for the liquid phase experiments) or as a diluent (in the gaseous experiments). These two competing reactions are described by eq. 1 and 2.

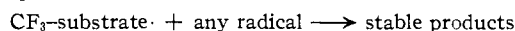


and the ratio of the respective rate constants k_2/k_1 was calculated by determining the ratios $\text{CF}_3\text{H}/\text{N}_2$ in experiments carried out in the presence and absence of the investigated substrate. It was shown¹ that k_2/k_1 is given by eq. 1

$$k_2/k_1 = (X_{\text{Hydr}}/X_{\text{Substr}}) \{ (\text{CF}_3\text{H}/\text{N}_2)_{\text{lost}} / (\text{CF}_3\text{H}/\text{N}_2)_{\text{formed}} \} \quad (1)$$

where X_{Hydr} and X_{Substr} are the mole fractions of the aliphatic hydrocarbon and the substrate in the investigated mixture, $(\text{CF}_3\text{H}/\text{N}_2)_{\text{formed}}$ denotes the ratio of these two products formed in the pertinent experiment and $(\text{CF}_3\text{H}/\text{N}_2)_{\text{lost}}$ represents the difference between the $(\text{CF}_3\text{H}/\text{N}_2)_{\text{formed}}$ and the $\text{CF}_3\text{H}/\text{N}_2$ found in a blank, *i.e.*, in an experiment carried out in the absence of the substrate.

In derivation of eq. 1, it was tacitly assumed that the addition, $\text{CF}_3 + \text{substrate} \rightarrow \text{CF}_3\text{-substrate}$, is irreversible. Were this process reversible, then a fraction of CF_3 radicals, initially combined with the substrate, would eventually yield an additional amount of CF_3H through the irreversible hydrogen abstraction 1. The hypothetical dissociation of the adduct radical has to compete with the radical-radical interactions



and these remove the adduct from the system. Therefore, if the dissociation is an important step in the overall process, then the ratio $\text{CF}_3\text{H}/\text{N}_2$ would depend on the concentration of the azo compound or on the intensity of the actinic light. Hence, for a constant ratio $X_{\text{Hydr}}/X_{\text{Substr}}$, an increase in the ratio $\text{CF}_3\text{H}/\text{N}_2$ arising from a decrease in the azo compound concentration, or from the diminished intensity of light, would manifest the reversibility of CF_3 addition.

Alternatively, the reversibility of CF_3 addition could be studied by investigating the coupling of this radical with a *trans* or *cis* isomer of a suitable substrate. The decomposition of the resulting adduct radical should lead to isomerization of the initial substrate. This technique was successfully applied by many investigators, *e.g.*, Wachholtz,^{5a} Ketelaar,^{5b} Waters,⁶ Noyes,^{7a,b} etc. The isomerization caused by a reversible Br or I atom addition is extremely rapid since the splitting of such atoms is very fast. In fact, such a dissociation may be faster than the rate of the internal rotation around the C-C bond of the respective adduct radical (see, *e.g.*, ref. 7a,b). The strength of a C-Cl bond is greater than that of C-Br or C-I; therefore, the isomerization arising from its reversible addition is slower. Nevertheless, a long kinetic chain of isomerization may accompany the addition of Cl atoms.

To test to what extent the addition of CF_3 radicals might be reversible, we decided to investigate their reactions with substrates which form relatively weak $\text{CF}_3\text{-substrate}$ bonds. The following compounds were chosen: benzene, *cis*- and *trans*-dichloroethylenes, diethyl fumarate, diethyl maleate and tetramethylethylene. These substrates were acquired commercially and their purity tested by v.p.c. The preparation and purification of hexafluoroazomethane was described in ref. 1, the technique of solution photolysis was reported in ref. 1 and 2 and that applied in the gaseous experiments in ref. 4.

Results and Discussion of Experiments Performed in Solution.—Two series of experiments were carried out in solution. In one the concentration of the azo

(5) (a) F. Wachholtz, *Z. physik. Chem.*, **125**, 1 (1927); (b) J. A. A. Ketelaar, P. F. VanVelden, G. H. J. Broers and H. R. Gersmann, *J. Phys. Colloid Chem.*, **55**, 987 (1951).

(6) D. H. Derbyshire and W. A. Waters, *Trans. Faraday Soc.*, **45**, 749 (1949).

(7) (a) R. M. Noyes, R. G. Dickenson and V. Schomaker, *J. Am. Chem. Soc.*, **67**, 1319 (1945); (b) H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952).

compound was varied while $X_{\text{Hydr}}/X_{\text{Substr}}$ was kept constant, whereas in the other $[\text{CF}_3\text{N}_2\text{CF}_3]$ was constant and the ratio $X_{\text{Hydr}}/X_{\text{Substr}}$ was varied. All these experiments were performed in isoöctane at 65°.

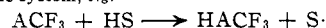
The relevant results are collected in Table I and their inspection shows that for a constant ratio $X_{\text{Hydr}}/X_{\text{Substr}}$, both the $\text{CF}_3\text{H}/\text{N}_2$ ratio and k_2/k_1 remain constant in spite of a tenfold change in the concentration of the azo compound. This indicates that in solution and at 65° the CF_3 addition is not reversible.⁸ It is interesting to notice that this conclusion applies to a series of compounds, for which the reactivities vary by a large factor; the lowest values for k_2/k_1 were found for benzene and *cis*-dichloroethylene (6-7) and the largest for tetramethylethylene (~500).

In a few experiments the photolysis of hexafluoroazomethane was carried out in pure *cis*- or *trans*-dichloroethylene, and the material analyzed on V.P.C. for the presence of its isomer. No isomerization was observed. However, such experiments may not be conclusive since the concentration of the azo compound was very low⁹ (10^{-3} – 10^{-2} M), and the de-energization of the vibrationally excited adduct would be fast. It was therefore decided to repeat these experiments in the gas phase, since higher ratios of $[\text{CF}_3\text{N}_2\text{CF}_3]/[\text{CHCl}=\text{CHCl}]$ could then be attained and the lifetime of the vibrationally excited adduct would be much longer.

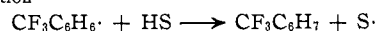
Photolysis in the Gas Phase.—A series of experiments was carried out in the gas phase, at 65° and at 150 or 160°, using the technique described by Dixon and Szwarc.⁴ *trans*-Dichloroethylene and benzene were the substrates and 2,3-dimethylbutane the diluent. The concentration of hexafluoroazomethane was varied by a factor of 5 and 10, respectively, while the ratio $[2,3\text{-dimethylbutane}]/[\text{substrate}]$ was kept constant. The results, shown in Table II, demonstrate that in the experiments involving *trans*-dichloroethylene, the ratio $\text{CF}_3\text{H}/\text{N}_2$ remains constant and independent of the azo compound concentration at both temperatures (65° and 160°). Hence, the addition of CF_3 radicals to dichloroethylene is irreversible in the gas phase even at 160°. In the system benzene + CF_3 , the data obtained at 65° show that this addition is also irreversible in the gas phase at the lower temperature; however, at 150° the ratio $\text{CF}_3\text{H}/\text{N}_2$ clearly increases with decreasing concentration of the azoethane. This indicates that the decomposition $\text{C}_6\text{H}_6\text{CF}_3 \rightarrow \text{C}_6\text{H}_6 + \text{CF}_3$ becomes noticeable at higher temperature—a not surprising observation in view of the presumably low dissociation energy of the $\text{C}_6\text{H}_6\text{-CF}_3$ bond.

The experiments carried out in the absence of the diluent showed that 4 mole % of hexafluoroazomethane photolyzed for 48 hr. in the vapor of *trans*-dichloroethylene (at 65°) isomerized this compound completely; v.p.c. analysis showed the ratio of the isomers in the starting material to be 99 (*trans*)/1 (*cis*), while the final material contained only 40–46% of the *trans* isomer and 54–60% of the *cis*. An identical experiment performed

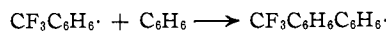
(8) If all the radicals ACF_3 disappear through reactions involving molecules present in the system, *e.g.*



then the change in the azo compound concentration would not affect the ratio $\text{CF}_3\text{H}/\text{N}_2$. However, this is unlikely. For example, the radicals formed from the addition to benzene are not sufficiently reactive to undergo either the reaction



or



(see also Table II). Moreover, the work of DeTar (D. F. DeTar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958)) proves that even at very low stationary concentration of radicals the $\text{RC}_6\text{H}_5 \cdot$ radicals do combine.

(9) The conditions imposed by our technique do not allow us to increase the concentration of the azo compound above 10^{-2} M in solution and above 70×10^{-3} mole/l. in the gas phase.

TABLE I

Solvent, isoöctane; $T = 65^\circ$				
[CF ₃ N ₂ CF ₃], moles/l. $\times 10^3$	(CF ₃ H/ N ₂) _{formed} ^b	(CF ₃ H/ N ₂) _{lost} ^b	$\frac{X_{Hydr}}{X_{Substr}}$	$\frac{k_2}{k_1}$
Benzene ^a				
2.94	0.155	0.184	6.38	7.57
5.33	.154	.185	6.38	7.65
9.65	.156	.183	6.38	7.51
21.5	.159	.180	6.38	7.22
30.2	.158	.181	6.38	7.31
Average of experiments described in ref. 2 7.1 ± 0.3				
<i>cis</i> -Dichloroethylene ^a				
3.13	0.153	0.121	8.33	6.61
5.66	.155	.119	8.33	6.41
10.25	.155	.119	8.33	6.41
22.3	.159	.116	8.33	6.08
31.2	.152	.123	8.33	6.72
~10	.336	.143	14.2	6.05
~10	.308	.171	12.1	6.70
~10	.296	.183	10.6	6.56
~10	.286	.192	9.4	6.28
~10	.260	.219	8.35	7.02
<i>trans</i> -Dichloroethylene ^a				
3.07	0.122	0.134	11.3	12.4
5.55	.123	.132	11.3	12.1
10.1	.123	.133	11.3	12.2
20.5	.111(?)	.143(?)	11.3	14.4(?)
28.7	.126	.129	11.3	11.6
~10	.252	.022	132	11.4
~10	.230	.043	66.3	12.5
~10	.213	.060	44.2	12.5
~10	.202	.072	33.1	11.9
10	.185	.089	26.5	12.7
10	.149	.154	12.3	12.7
10	.130	.173	10.1	13.4
10	.110	.193	7.33	12.8
10	.097	.206	5.66	12.0
Diethyl fumarate ^a				
3.07	0.240	0.270	86.6	97.4
10.05	.255	.255	86.6	86.6
12.8	.252	.258	86.6	88.6
18.0	.249	.261	86.6	90.7
~10	.228	.081	213	75.8
~10	.174	.135	106	82.0
~10	.137	.173	70.2	88.7
~10	.117	.192	52.5	86.6
~10	.100	.209	41.8	87.2
Diethyl maleate ^a				
3.33	0.333	0.206	47.3	29.3
5.66	.396(?)	.143(?)	47.3	17(?)
10.25	.339	.200	47.3	27.9
13.1	.345	.194	47.3	26.6
18.3	.330	.209	47.3	29.9
~10	.238	.071	92.6	27.8
~10	.199	.110	45.8	25.2
~10	.162	.148	30.2	27.6
~10	.143	.166	22.4	26.0
~10	.123	.186	17.7	26.9
Tetramethylethylene ^a				
3.19	0.200	0.216	517	559
5.77	.204	.212	517	540
10.5	.201	.215	517	554
20.7	.208	.208	517	517
29.0	.207	.209	517	522
~10	.167	.099	957	566
~10	.157	.109	736	518
~10	.123	.143	480	558
~10	.100	.166	318	528
~10	.072	.194	191	515

^a Substrate. ^b The ratios (CF₃H/N₂)_{formed} and (CF₃H/N₂)_{lost} are given in arbitrary units (ratio of peak heights on the respective chromatograms). It was found that such a procedure gives reliable values for (CF₃H/N₂)_{lost}/(CF₃H/N₂)_{formed} and hence was adopted here for the sake of expediency.

TABLE II

PHOTOLYSIS OF CF₃N₂CF₃ IN THE GAS PHASE

CF ₃ N ₂ CF ₃ , moles $\times 10^5$	Me ₂ CH- CHMe ₂ , moles $\times 10^5$	<i>trans</i> - CHCl=CHCl, moles $\times 10^5$	CF ₃ H/ N ₂	$\frac{k_2}{k_1}$
1.29	3920	..	1.85	..
1.29	3920	..	1.82	..
0.675	3070	1450	0.755	3.00
1.55	3070	1450	.775	2.92
3.82	3070	1450	.756	3.00
6.77	3070	1450	.728	3.17
Average 3.02				
$T = 160^\circ$				
1.20	2110	..	2.00	..
0.534	2110	980	0.94(?)	2.40(?)
1.20	2110	980	1.02	2.06
3.13	2110	980	1.02	2.06
5.66	2110	980	1.03	2.01
Average 2.06				
$E_2 - E_1 = -1.7$ kcal./mole; $A_2/A_1 = 0.3$				
CF ₃ N ₂ CF ₃ , moles $\times 10^5$	Me ₂ CH- CHMe ₂ , moles $\times 10^5$	Benzene, moles $\times 10^5$	CF ₃ H/ N ₂	$\frac{k_2}{k_1}$
1.29	561	..	1.80	..
0.248	561	529	0.835	1.23
1.54	561	529	.823	1.27
2.56	561	529	.850	1.19
Average 1.23				
$T = 150^\circ$				
1.4	1860	..	2.05	..
1.07	1860	1780	1.15	0.79
1.83	1860	1780	1.10	.89
6.40	1860	1780	1.05	.96
10.1	1860	1780	1.01	1.05

in the absence of the azo compound produced only 7% of the *cis* isomer during 48 hr. of photolysis. It is obvious therefore that the photolysis led to a long chain of isomerization initiated directly or indirectly by the photodecomposition of hexafluoroazomethane.

Since the results of these experiments contradict the conclusion based on the kinetic findings (see Table II), it was necessary to check whether the isomerization does not result from preferential quenching of excited molecules of the azo compound by dichloroethylene. The results of these tests are summarized in Table III and show that dichloroethylene does not quench excited CF₃N₂CF₃ any more efficiently than 2,3-dimethylbutane. Moreover it is important to notice that no isomerization took place in the mixture of dichloroethylene and 2,3-dimethylbutane, and this observation provides perhaps the best argument against the dissociation.

The contradictory evidence reported above may be reconciled if one assumed that the vibrationally excited adduct radical formed in reaction 2 decomposes rapidly into Cl atom and CF₃CH=CHCl (3)



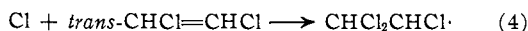
but not into CF₃ + CHCl=CHCl. The chlorine atom initiates the chain isomerization through the sequence of reactions 4 and 5.

TABLE III

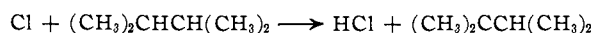
PHOTOLYSIS OF HEXAFLUOROAZOMETHANE IN THE GAS PHASE AT 65°

<i>trans</i> -CHCl=CHCl, × 10 ⁵ mole	2,3-DMB × 10 ⁵ moles	Time of phot., hr.	N ₂ × 10 ⁵ moles	CF ₃ H in the product	<i>trans/cis</i> in the product
{ 1980	0	3	2.85	0	93/7
{ 0	2300	3	2.20	3.86	..
{ 1930	0	6	5.46	0	...
{ 0	2300	6	3.76	6.82	...
{ 1960	0	9	6.98	0	85/15
{ 0	2300	9	5.14	9.28	...
{ 1430	1980	6	4.46	.. ^a	99/1
{ 1395	0	6	6.70	..	75/25
{ 1330	1920	12	6.30	.. ^a	99/1
{ 1330	0	12	11.5	...	72/28

^a HCl identified in the products. In these experiments [CF₃N₂CF₃] varied between 20 and 30 × 10⁻⁵ mole.



This mechanism is supported by two observations: (1) HCl was identified as a by-product of the reaction both in the presence and in the absence of 2,3-dimethylbutane. (2) The addition of 2,3-dimethylbutane suppressed the isomerization (see Table III). Under these conditions the free chlorine atoms are removed by the reaction

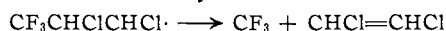


and thus the isomerization chain is interrupted.

General Discussion

The addition of an atom or free radical to an olefin produces a vibrationally excited adduct radical which contains all the energy of the newly formed bond and the activation energy required for the reaction. Such a radical may decompose without requiring any activation energy or it may be deactivated by a suitable collision.¹⁰ Its lifetime might be substantially longer than the period of internal rotation around the C-C bond and, if this is the case, the isomerization ensues. The work of Dainton¹⁰ shows that such a situation arises in the addition of Cl atoms to the dichloroethylenes, and therefore the isomerization observed in our experiments is explicable if it is caused by Cl atoms.

The question arises why the dissociation



is not observed under conditions which permit the rapid dissociations (3) and (5). One could argue that the C-Cl bond is weaker than the C-CF₃ bond, and therefore the former is ruptured preferentially. Our knowledge of the bond dissociation energies is not sufficiently precise to argue this point. On the whole, the C-Cl bond dissociation energies in radicals such as CHCl₂CHCl·, are of the order of 20 kcal./mole (see, e.g., ref. 10), and similar values were derived for C-C bond dissociation energies in hydrocarbon radicals, e.g., $D(\cdot\text{CH}_3\text{CH}_2-\text{CH}_3) \approx 25$ kcal./mole.¹¹ The CF₃-C bond dissociation energies do not appear to differ to any extent from those of CH₃-C and hence

it is probable that $D(\text{CF}_3-\text{CHClCHCl}\cdot)$ may be slightly higher than $D(\text{Cl}-\text{CH}(\text{CF}_3)\text{CHCl}\cdot)$.

The work of Cvetanovic¹² demonstrated a similar dissociation of a vibrationally excited ethyl radical in

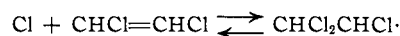
(10) P. B. Ayscough, A. J. Cocker and F. S. Dainton, *Trans. Faraday Soc.*, **58**, 284 (1962).

(11) M. Szwarc, *Discussions Faraday Soc.*, **10**, 143 (1951).

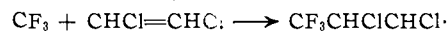
(12) A. H. Turner and R. J. Cvetanovic, *Can. J. Chem.*, **37**, 1075 (1959).

which fission of a relatively strong C-H bond takes place. Moreover, he noticed that the addition of an H atom to C₂D₄ does not lead to an exchange, while an exchange readily takes place when a D atom adds to C₂H₄. Cvetanovic concluded that the higher C-D bond dissociation energy endows the hot C₂H₄D radical with enough energy to rupture the weaker C-H bond, whereas the hot C₂D₄H radical has 1 kcal./mole less energy and cannot break the 1-kcal./mole stronger C-D bond to afford an exchange. This small difference seems to be sufficient to produce an appreciable effect in one case and lack of an effect in the other.

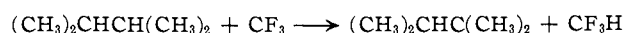
Nevertheless, the energetic considerations seem insufficient to explain the reversibility of the reaction



and lack of reversibility in the reaction



For example, the addition of CF₃ radicals to tetramethylethylene was investigated in the gas phase at 65° and no formation of methane was observed. It is probable that $D(\text{CF}_3-\text{C})$ is slightly greater than $D(\text{CH}_3-\text{C})$, but neither bond seems to rupture in this process. It seems that the rupture of a C-R bond, where R is a polyatomic moiety, requires a more detailed energy distribution than the fission of a C-X bond where X is an atom. Indeed, one anticipates various conditions to be imposed upon the geometry, and perhaps also on the conformation, of the polyatomic R moiety in the transition state, while such conditions are irrelevant in the fission of a C-X bond. Of course, a fission of the C-C bond in radicals is observed at higher temperatures, e.g., in studies of Martin,¹³ Gordon,¹⁴ Steacie,¹⁵ etc. Also in our work it was observed that radicals such as (CH₃)₂CCH(CH₃)₂, formed as result of the reaction



partially decompose into CH₃ + (CH₃)₂C:C(CH₃)₂ at temperatures higher than 130°. Such a decomposition is thermal and not of a vibrationally excited radical.

To demonstrate that the rate constant of CF₃ radical addition to the *trans*-dichloroethylene is "normal," we reinvestigated this reaction in 2,3-dimethylbutane, as well as in isoöctane. The results are given in Tables I and IV. From these data the ratio $k_{1(2,3\text{-DMB})}/k_{1(\text{isoöctane})}$ may be calculated as 4.7. Similar values are derived from the data reported by Dixon and Szwarc⁴; namely, $k_{1(2,3\text{-DMB})}/k_{1(\text{isoöctane})}$ was found to be 4.1 (using vinyl chloride), 6.7 (using 2-fluoropropane), 4.7 (vinyl fluoride), etc. Studies of Dixon and Szwarc⁴ showed that $(k_2/k_1)_l/(k_2/k_1)_g$ varies from 1.6 to 2.2 for halogenated olefins in 2,3-dimethylbutane. The results reported in Tables II and IV give the ratio $(k_2/k_1)_l/(k_2/k_1)_g = 1.5$ for the same diluent.

Reactivities of Chlorinated Olefins and Some Other Substrates toward CF₃ Addition.—The results shown in Table V are of some interest. The relative rate constants of CF₃ addition to *cis*- and *trans*-dichloroethylenes are 6.5 and 12.5, respectively. Since the *cis* isomer is thermodynamically more stable, this gradation in reactivities is not surprising. However, as has been reported earlier,¹ the *cis*- and *trans*-butene-2's are equally reactive in spite of the fact that the *trans* isomer is more stable than the *cis*. The considerable difference in the reactivity of diethyl maleate and diethyl fumarate has been expected. Its significance was

(13) R. W. Durham, G. R. Martin and H. C. Sutton, *Nature*, **164**, 1052 (1949).

(14) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **79**, 5902 (1957).

(15) G. O. Pritchard and E. W. R. Steacie, *Can. J. Chem.*, **35**, 1216 (1957).

TABLE IV
ADDITION OF CF₃ TO *trans*-DICHLOROETHYLENE AT 65°

CF ₃ H/N ₂	X _{Hydr} /X _{Substr}	k ₂ /k ₁
0.499	No substr.	..
.510	No substr.	..
.507	No substr.	..
.276	3.51	2.90
.276	3.51	2.90
.274	3.51	2.95
.277	3.51	2.91
Average		2.92

discussed by Lewis and Mayo,¹⁶ who explained the low reactivity of diethyl maleate by its non-coplanarity.

TABLE V

THE RELATIVE RATE CONSTANTS (*k*₂) OF CF₃ RADICAL ADDITION AT 65° IN ISOÖCTANE

*k*₁ denotes the rate constant of the reaction CF₃ + isoöctane → CF₃H + isoöctyl radical

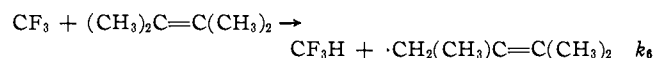
Substrate	No. of expt.	Range of X _{Hydr} /X _{Substr}	k ₂ /k ₁
<i>cis</i> -Dichloroethylene	10	8-14	6.5 ± 0.6
<i>trans</i> -Dichloroethylene	14	5-132	12.5 ± .5
Trichloroethylene	5	2-13	12.8 ± .8
Tetrachloroethylene	4	0.3-2	1.3 ± .4
Diethyl maleate	12	17-92	26.7 ± 1.0
Diethyl fumarate	14	41-213	85 ± 6.0
Tetramethylethylene	10	190-960	538 ± 15

The electrophilic nature of CF₃ radicals is clearly demonstrated by the low reactivity of the dichloroethylenes and tetrachloroethylene which contrasts with the high reactivity of the butene-2's and tetramethylethylene. The presence of Cl atoms or CH₃ groups on the reactive center introduces a steric hindrance

(16) F. M. Lewis and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1533 (1948).

which reduces the rate of CF₃ addition to tetrachloroethylene or tetramethylethylene. In the former compound the polar effect reduces the reactivity even more, while in the latter the opposite polar effect more than compensates for the steric hindrance making tetramethylethylene slightly more reactive than ethylene.¹ It should be pointed out that the mesomeric effect of a Cl atom on the β-carbon enhances the reactivity of the olefin¹⁷; the *k*₂/*k*₁ for vinyl chloride was found to be 273 and for vinylidene dichloride 509. This effect explains the relative reactivity of trichloroethylene.

Finally, some photolytic experiments carried out in pure tetramethylethylene should be mentioned. The small amounts of CF₃H produced in such experiments were attributed to the reaction



which competed with reaction 2. On the other hand C₂F₆ formed in such a process is believed to represent the result of the cage recombination of CF₃ radicals. The results of three experiments carried out at 65° led to the following average values for the respective ratios: C₂F₆/N₂ = 0.204 and CF₃H/N₂ = 0.008. Accepting the interpretation given above we deduce therefore that *k*₆/*k*₂ for tetramethylethylene is 0.005. Since *k*₂/*k*₁ = 538, it follows that *k*₆/*k*₁ = 2.7, *i.e.*, the rate constant *k*₆' of H abstraction from tetramethylethylene *per active H* is 0.23 of that of H abstraction from isoöctane. Similar experiments carried out in toluene and in mesitylene³ led to *k*₆'/*k*₁ ratios of 0.12 and 0.14, respectively.

Acknowledgment.—We wish to thank the National Science Foundation and the Wright-Patterson Air Research and Development Command for financial support of this investigation.

(17) Unpublished results from this Laboratory.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, N. J.]

Kinetics of Proton Transfer in Methanol for a Series of Carboxylic Acids of Varying Strength

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RECEIVED JANUARY 9, 1963

It has been shown previously that in methanol containing benzoic acid and sodium benzoate, the rate of proton exchange in reactions involving these solutes is given at room temperature by: $R_M = k_1[\text{HBz}] + k_2[\text{HBz}][\text{NaBz}]$. The *k*₁-process was found to involve two methanol molecules and a cyclic reaction mechanism; the *k*₂-process was found to involve one methanol molecule. We now report n.m.r. measurements of *k*₁ and *k*₂ in methanol at 24.8° for a series of nitro-substituted benzoic acids in order to evaluate the sensitivity of these rate constants to acid strength. Values of *pK*_A, 10⁻⁵*k*₁ (sec.⁻¹) and 10⁻⁸*k*₂ (sec.⁻¹ M⁻¹) are, respectively: benzoic, 9.41, 1.31, 1.21; *m*-nitrobenzoic, 8.34, 3.6, 2.5; *p*-nitrobenzoic, 8.33, 4.5, 2.7; *o*-nitrobenzoic, 7.56, 19, 1.8; 3,5-dinitrobenzoic, 7.38, 16, 4.1. Except for *o*-nitrobenzoic acid, plots of log *k*₁ or log *k*₂ vs. log *K*_A are nicely linear, the slopes being 0.53 for log *k*₁ and 0.26 for log *k*₂. The low sensitivity to acid strength obtained for the termolecular process represented by *k*₂ is consistent with a concerted reaction mechanism. The peculiar sensitivity obtained for the cyclic process represented by *k*₁ is too high to be consistent with a simple model for a concerted mechanism and too low to be consistent with a simple model for a two-step process involving an intimate ion pair intermediate.

In a preceding paper² the kinetics of proton exchange in buffered solutions of benzoic acid and sodium benzoate was studied in detail, using the nuclear magnetic resonance (n.m.r.) technique. It was found that the exchange of the hydroxyl protons of the solvent is catalyzed not only by methyloxonium ion and methoxide ion, but also by the buffer components. That is to say, the quantity *R*_M, defined by eq. 1, is greater than zero.

(1) Alfred P. Sloan Fellow, 1960-1961.

(2) E. Grunwald, C. F. Jumper and S. Meiboom, *J. Am. Chem. Soc.*, **85**, 522 (1963).

$$R_M = R - (k_{\text{MeOH}_2^+}[\text{MeOH}_2^+] + k_{\text{MeO}^-}[\text{MeO}^-]) \quad (1)$$

In eq. 1, *R* is the experimentally measured rate of proton exchange, and the quantity which is subtracted from *R* is the previously established rate law for proton exchange in the absence of buffer.³ Numerical values of the rate constants *k*_{MeOH₂⁺} and *k*_{MeO⁻} are available from the previous investigation.³

For data obtained at 25°, an analysis of *R*_M as a function of the formal concentrations of benzoic acid [HA]

(3) E. Grunwald, C. F. Jumper and S. Meiboom, *ibid.*, **84**, 4664 (1962).