

Interaction of Photoexcited Naphthalenes with Trifluoroacetic Acid¹

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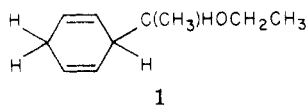
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The bimolecular hydrogen-exchange reaction of naphthalene with trifluoroacetic acid involves the singlet excited state of the hydrocarbon. Comparison of the efficiency of fluorescence quenching of naphthalene by trifluoroacetic acid with the effect of the acid in promoting hydrogen exchange indicates that the initial interaction of trifluoroacetic acid with excited naphthalene affords a π complex, which is 100 times more likely to collapse to ground-state reactants than to proceed to isotopically exchanged products. The trifluoroacetic acid assisted photodecomposition of 1-chloronaphthalene is also a singlet state reaction. It is believed to involve protonation of the excited halide, followed by electron transfer from the solvent, ether. Support for this mechanism was obtained by showing that other solvents whose ionization potentials are comparable with that of ether promote similar photochemistry.

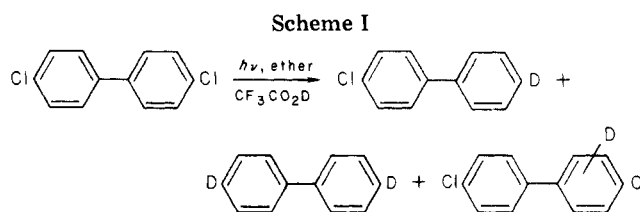
Trifluoroacetic acid (TFA) has featured in a number of photoreactions of aromatic compounds in recent years. Lodder and Havinga² studied the hydrogen isotope exchange reaction of simple aromatic compounds with TFA, using alkanes as solvents. Hydrogen exchange was rather inefficient, but a plot of ϕ_{ex}^{-1} vs. $[\text{TFA}]^{-1}$ was linear. They suggested that the reaction might be a bimolecular photoelectrophilic substitution. Seemingly different results were obtained by Mason and Smith,³ who found no hydrogen exchange when aromatic hydrocarbons were illuminated in aqueous perchloric acid.

Bryce-Smith and Cox⁴ studied the photoaddition of ether to benzene, a reaction catalyzed by TFA. Other acids were ineffective as catalysts. They suggested^{4,5} that TFA protonates an excited state of benzene and that this is followed by electron transfer from ether, eventually affording the adduct 1.



Most recently, Nordblom and Miller⁶ reported that the photodechlorination of 4,4'-dichlorobiphenyl is catalyzed by TFA in ether as solvent. Other solvents, such as alcohols or cyclohexane, did not show this effect and neither did other organic acids such as acetic acid. There appeared to be a kinetic isotope effect for the reaction, for when deuterated TFA was used in place of $[^1\text{H}]\text{TFA}$, most of the catalytic effect disappeared.

Our initial interest was directed to this last report, on account of our previous studies on the photodecomposition of chlorinated biphenyls.⁷ We repeated the experiment of Nordblom and Miller and discovered that when 4,4'-dichlorobiphenyl is illuminated with deuterated TFA in ether, deuterium replaces the chlorine that is lost; i.e., the hydrogen in the reduced product comes from TFA rather than from the solvent (Scheme I). Simultaneously, however, H-D exchange is seen in the recovered starting material. It therefore seemed that the "photoelectrophilic" hydrogen exchange and the acid-catalyzed photodechlorination might be related. We have attempted, in this work, to discover what mechanistic links may exist between

Table I. Isotope Effects for Fluorescence Quenching of Aromatic Molecules by TFA in Isooctane^a

compd	$k_q\tau, \text{M}^{-1}$	
	$\text{CF}_3\text{CO}_2\text{H}$	$\text{CF}_3\text{CO}_2\text{D}$
naphthalene	15.6	14.0
1-fluoronaphthalene	10.6	8.0
1-chloronaphthalene	1.8	1.1
biphenyl	23.2	20.6
4,4'-dichlorobiphenyl	3.3	3.0

^a Aerated solutions, 23 °C.Table II. Fluorescence Quenching of Substituted Naphthalenes by TFA^a

substituent	$k_q\tau, \text{M}^{-1}$	τ, ns	$k_q, \text{L mol s}^{-1}$
none	15.6	96	1.6×10^8
1-CH ₃	26.8	67	4.0
2-CH ₃	22.0	59	3.7
1-F	10.6	39	2.7
2-F	8.0	18	5.6
1-Cl	1.8	2.4	7.5
2-Cl	1.6	4.2	3.9
1-OCH ₃	58	25	23
2-OCH ₃	64	11	58

^a In aerated solutions of isooctane, 23 °C. ^b Reference 8.

the reactions reported in ref 2, 4, and 6, especially in view of their very specific requirements of experimental conditions.

Hydrogen Exchange of Naphthalene Using TFA-Isooctane. Exchange was shown to be a singlet-state process, in that benzophenone failed to sensitize the exchange with naphthalene, a substance for which triplet energy transfer from benzophenone is efficient. Correspondingly, TFA quenched the fluorescence of naphthalene (and many other substances) in isooctane. However, weaker acids, such as acetic acid, were ineffective at quenching the fluorescence.

Using the Stern-Volmer method, we observed a small deuterium isotope effect for fluorescence quenching for a number of molecules (Table I). This shows that hydrogen transfer is intimately involved with fluorescence quenching. However, we do not believe that the fluorescence is

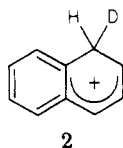
(1) Presented in part at the IX International Conference on Photochemistry, Cambridge, England, 1978.

(2) G. Lodder and E. Havinga, *Tetrahedron*, **28**, 5583 (1972).(3) S. F. Mason and B. E. Smith, *J. Chem. Soc. A*, 325 (1969).(4) D. Bryce-Smith and G. B. Cox, *Chem. Commun.*, 915 (1971).(5) D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **33**, 2459 (1977).(6) G. D. Nordblom and L. L. Miller, *J. Agric. Food Chem.*, **22**, 57 (1974).(7) N. J. Bunce, Y. Kumar, L. Ravanal, and S. Safe, *J. Chem. Soc., Perkin Trans.* **2** 880 (1978).

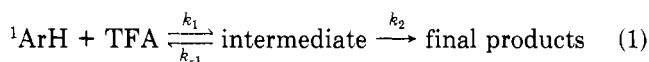
Scheme II. Mechanistic Models for Hydrogen Exchange

model	TFA dependence of		
	fluorescence quenching	quantum yield	
I	${}^1\text{ArH} + \text{TFA} \xrightarrow{k_1} \text{products}$	$\left(\frac{\phi^0}{\phi}\right)_\tau = 1 + k_1\tau[\text{TFA}]$	$\frac{1}{\phi_{\text{ex}}} = 1 + \frac{1}{k_1\tau[\text{TFA}]}$
II	${}^1\text{ArH} + \text{TFA} \xrightleftharpoons[k_{-1}]{k_1} \text{X} \xrightarrow{k_2} \text{products}$	$\left(\frac{\phi^0}{\phi}\right)_\tau = 1 + \frac{k_1k_2}{k_{-1} + k_2}\tau[\text{TFA}]$	$\frac{1}{\phi_{\text{ex}}} = 1 + \frac{k_{-1} + k_2}{k_1k_2\tau[\text{TFA}]}$
III	${}^1\text{ArH} \xrightarrow{k_1} \text{X} \begin{cases} \xrightarrow{k_2} \text{ArH} \\ \xrightarrow[k_3]{\text{TFA}} \text{products} \end{cases}$	no quenching	$\frac{1}{\phi_{\text{ex}}} = \left(1 + \frac{1}{k_1\tau}\right) \left(\frac{k_2 + k_3[\text{TFA}]}{k_3[\text{TFA}]}\right)$
IV	${}^1\text{ArH} + \text{TFA} \xrightarrow{k_1} \text{X} \begin{cases} \xrightarrow{k_2} \text{ArH} \\ \xrightarrow[k_3]{} \text{products} \end{cases}$	$\left(\frac{\phi^0}{\phi}\right)_\tau = 1 + k_1\tau[\text{TFA}]$	$\frac{1}{\phi_{\text{ex}}} = \frac{k_2 + k_3}{k_3} \left\{1 + \frac{1}{k_1\tau[\text{TFA}]}\right\}$
V	${}^1\text{ArH} + \text{TFA} \xrightleftharpoons[k_{-1}]{k_1} \text{X} \begin{cases} \xrightarrow{k_2} \text{ArH} \\ \xrightarrow[k_3]{} \text{products} \end{cases}$	$\left(\frac{\phi^0}{\phi}\right)_\tau = 1 + \frac{k_1(k_2 + k_3)}{(k_{-1} + k_2 + k_3)}\tau[\text{TFA}]$	$\frac{1}{\phi_{\text{ex}}} = \left(\frac{k_2 + k_3}{k_3}\right) + \left(\frac{k_{-1} + k_2 + k_3}{k_1k_3\tau[\text{TFA}]}\right)$

quenched due to the immediate production of a σ complex such as **2**. For a series of naphthalene derivatives whose



singlet lifetimes were already known,⁸ there is essentially no substituent effect on fluorescence quenching, even though the quenching rates are well below the rate of diffusion. These results are in Table II. (The two methoxynaphthalenes are exceptional, but here protonation is occurring at oxygen rather than at the ring.⁹) Two possible explanations for the lack of substituent effect can be advanced: quenching does not lead to a σ intermediate such as **2** and/or quenching is a reversible process. If quenching is reversible (eq 1) then the Stern-Volmer



constant for fluorescence quenching becomes $k_1k_2(k_{-1} + k_2)^{-1}\tau$ rather than simply $k_1\tau$. The interplay of k_1 , k_{-1} , and k_2 with substituent might thus erase any substituent effect on k_1 .

Further kinetic arguments support our contention that quenching does not lead directly to a σ intermediate. We noted above that Lodder and Havinga obtained linear plots of ϕ_{ex}^{-1} vs. $[\text{TFA}]^{-1}$. This indicates a bimolecular reaction involving TFA and excited ArH. Knowing that the reaction involves the singlet excited state of ArH, we can compare the Stern-Volmer fluorescence quenching constant and the slope of the ϕ_{ex}^{-1} vs. $[\text{TFA}]^{-1}$ plot. The outcomes for several mechanistic possibilities are shown in Scheme II.

Experimentally, the Stern-Volmer constant for fluorescence quenching is 15.6 M^{-1} in the case of naphthalene (14.0 M^{-1} when $\text{CF}_3\text{CO}_2\text{D}$ is the quencher). If either of mechanisms I or II are followed, the slope of the

plot of ϕ_{ex}^{-1} vs. $[\text{CF}_3\text{CO}_2\text{D}]^{-1}$ should be the reciprocal of this, viz. 0.07 M . The actual value is larger by a factor of almost 100. This means that fluorescence quenching is a much more efficient process than hydrogen exchange and excludes direct formation of a symmetrical intermediate as in mechanisms I and II.

Possible mechanisms allowing for this inefficiency of hydrogen exchange are given as III-V in Scheme II. Mechanism III and its relatives may be dismissed at once; the intermediate which can return to ground-state ArH cannot precede the attack by TFA; otherwise no fluorescence quenching is observed. Both mechanisms IV and V satisfy the experimental observations; they postulate an intermediate which can return to ground state without hydrogen exchange (k_2) or go on to unchanged product (k_3). Since exchange is inefficient experimentally, it follows that $k_2 > k_3$.

We develop our argument for the simpler case, mechanism IV, where the initial quenching is assumed to be irreversible. The Stern-Volmer quenching of fluorescence thus affords $k_1\tau$. The intercept of the ϕ_{ex}^{-1} vs. $[\text{CF}_3\text{CO}_2\text{D}]^{-1}$ plot yields $(k_2 + k_3)/k_3$, which, since $k_2 > k_3$, approximates to k_2/k_3 . Our experimental values for this ratio are 68 and 105. The slope of this graph is 8.4 and 5.5 M from two runs; this compares with 4.9 and 7.5 M obtained by dividing the intercept by $k_1\tau$ obtained as the slope of the fluorescence quenching curve. Mechanism IV thus accounts for the experimental observations.

If the original quenching of the singlet naphthalene by TFA is reversible, similar results are obtained. The dependence of ϕ_{ex} with concentration can be written in the form of eq 2, stressing its similarity with the analogous

$$\frac{1}{\phi_{\text{ex}}} = \frac{k_2 + k_3}{k_3} \left(1 + \frac{1 + k_{-1}/(k_2 + k_3)}{k_1\tau[\text{TFA}]}\right) \quad (2)$$

relationship of mechanism IV. Again, the intercept of the plot of ϕ_{ex}^{-1} vs. $[\text{TFA}]^{-1}$ affords an approximation to k_2/k_3 . In principle, the comparison of the slope of this line with the slope of the fluorescence quenching plot indicates the importance of the "reverse quenching" reaction whose rate constant is k_1 . In practice our data are not precise enough to obtain this information. Thus either of mechanisms IV and V are compatible with our data.

(8) P. Lentz, H. Blume, and D. Schulte-Frohlinde, *Ber. Bunsenges. Phys. Chem.*, **74**, 484 (1970).

(9) B. E. Smith, *J. Chem. Soc. A*, 2673 (1969).

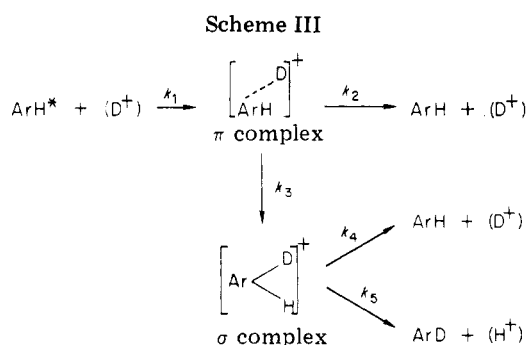


Table III. Solvent Effect on Quenching of Naphthalene Fluorescence by TFA

solvent	k_{qT} , M^{-1}	solvent	k_{qT} , M^{-1}
isooctane	15.6	acetonitrile	0.6
benzene	10.0	dioxane	no quenching
1-octene	2.8	ether	no quenching
tetrachloroethylene	0.8	ethanol	no quenching

It follows that intermediate X is a species that has a hydrogen (deuteron) bonded to the excited naphthalene moiety. However, this incoming hydrogen is bonded much more loosely than the ring hydrogens already present, for it is lost about 100 times more readily ($k_2 > k_3$). We therefore might describe it as a π complex. This would be consistent with the rather small kinetic isotope effects seen in Table I. The proposed mechanism is summarized in Scheme III. Strictly, of course, one cannot equate k_3 with the rate constant for product formation in mechanism IV; but since we expect an isotope effect such that $k_5 > k_4$, no serious error should be introduced.

Solvent Effects on Hydrogen Exchange. We noted above that Mason and Smith found no photochemical hydrogen exchange in $H_2O/HClO_4$ as the acidic medium.³ They also failed to detect fluorescence quenching. We have studied the fluorescence quenching of naphthalene by TFA in various solvents (Table III). The failure to detect quenching in certain solvents is curious in the light of the conclusion of Kuz'min et al.¹⁰ that the singlet excited states of aromatic hydrocarbons are strong bases, so that proton transfer from TFA should be highly favorable.

The trend in quenching efficiency in Table III is not with solvent polarity, as judged by bulk dielectric constant, but with basicity. The weaker the base, the more efficient the fluorescence quenching. Although none of these solvents is basic enough to accept the proton of TFA to a significant extent, the more basic ones should stabilize TFA by hydrogen bonding.

Studies on ground-state proton transfer have revealed that proton transfer involving carbon often requires considerable activation energy, even if the process is thermodynamically favored. We interpret our results in these terms. Proton transfer to afford the π complex has an activation energy which is larger in solvents where the TFA is stabilized by solvation. In this situation, proton transfer becomes unlikely during the lifetime of the singlet excited state. This interpretation is supported by the existence of a kinetic isotope effect in fluorescence quenching.

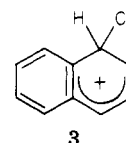
Such an explanation can account for the uniqueness of TFA in promoting hydrogen exchange. Weaker acids, such as acetic acid, do not quench the excited state of naphthalene (and other substances) nor do they bring about

exchange. Our interpretation would be that the activation energy to proton transfer is too high. TFA is unusual in being a strong Brønsted acid that is soluble in alkanes. We showed, however, that TFA is not unique in its behavior. Two other alkane-soluble and relatively strong acids, trichloroacetic acid and *p*-dodecylbenzenesulfonic acid, were both able to quench the fluorescence of naphthalene in isooctane solution. Hydrogen exchange could also be induced; for example, at a concentration of 0.1 M, *p*-dodecylsulfonic acid led to protium incorporation into $C_{10}D_8$ with a quantum efficiency of 0.05.

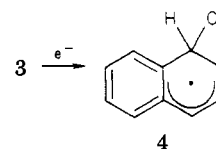
Studies on TFA-Assisted Photodechlorination of 1-Chloronaphthalene. This substrate was used because naphthalene had been studied for H-D exchange. It was first demonstrated that 1-chloronaphthalene behaved like 4,4'-dichlorobiphenyl. The reaction has the same features: accelerated decomposition by TFA in ether, but not in cyclohexane or alcohols, kinetic isotope effect, and incorporation of deuterium into both naphthalene and 1-chloronaphthalene when CF_3CO_2D is used.

Like the hydrogen-exchange reaction, the TFA-assisted dechlorination is a singlet-state process, no sensitization by benzophenone being observed. Fluorescence quenching of 1-chloronaphthalene by TFA is not detectable in ether, although it occurs in isooctane (Table I). The lack of fluorescence quenching in ether is not incompatible with a singlet-state reaction, because quantum yields of the assisted reaction are so low ($\sim 10^{-3}$).

A puzzling question was the mode of loss of chlorine following the presumed protonation. Loss of (Cl^+) from an intermediate such as **3** is very difficult.¹¹ We therefore



invoked the postulate of Bryce-Smith and Cox⁴ that proton transfer might be followed by electron transfer from the solvent. This would afford intermediate **4** from which loss of $Cl\cdot$ would be facile.



The ionization potential¹² of diethyl ether is about 9.5 eV; those of alkanes and of alcohols are almost 1 eV higher. We could therefore rationalize the unique behavior of ether in terms of its ionization potential being low enough to quench **3** (or the corresponding π complex) by electron transfer. (The ionization potential is not so low, however, that the excited aromatic compound is quenched directly, as, for example, by amines. Ether can apparently not quench the singlet state of 1-chloronaphthalene directly in that no fluorescence quenching by ether was observed in cyclohexane solutions, using ether in concentrations up to 3 M.)

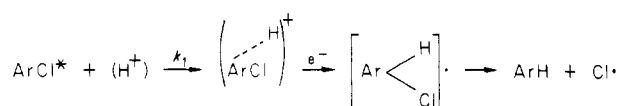
In order to test this point we chose two solvents of ionization potential very close to that of ether to use in place of ether. Tetrachloroethylene and 1-octene were selected. Dechlorination was studied in each solvent in the presence and absence of TFA. The quantum yield of

(11) C. L. Perrin, *J. Org. Chem.*, **36**, 420 (1971).

(10) M. G. Kuz'min, B. M. Uzhinov, and I. V. Berezin, *Russ. J. Phys. Chem. (Engl. Transl.)*, **41**, 222 (1967).

(12) Ionization potentials were taken from V. I. Vedenev, "Bond Energies Ionization Potentials and Electron Affinities", Arnold, London, 1966.

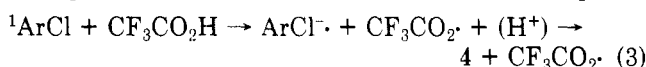
Scheme IV



decomposition of 1-chloronaphthalene was considerably enhanced in tetrachloroethylene-TFA compared with that in tetrachloroethylene alone. The corresponding experiment with 1-octene afforded smaller and irreproducible elevations of the quantum yield. The results are therefore consistent with the proposed role of ether as an electron-transfer agent.

Finally, we have shown that, as in the hydrogen-exchange reaction, TFA is not unique. *p*-Dodecylbenzenesulfonic acid also enhances the efficiency of photodecomposition of 1-chloronaphthalene in ether. Thus we can modify Scheme III to Scheme IV when the starting material is an aryl chloride. In this case we must infer the presence of the π complex, which can afford hydrogen exchange by the mechanism of Scheme III. It may be noted that Scheme IV provides a new mechanism for photodecomposition of aryl halides involving the intermediate 4. Previously, aryl halide photodecomposition has been interpreted either in terms of simple C-X bond homolysis or by way of electron transfer (e.g., in the presence of amines) followed by the decomposition of an aryl halide radical anion.¹³

Clearly, there are other mechanistic possibilities for arriving at the intermediate 4 or one similar. One such example would be electron transfer from TFA (eq 3).



Our prejudice is against this type of mechanism only because it allows no special role for ether or a solvent of comparable ionization potential.

Experimental Section

Compounds were reagent grade materials, except for isooctane, which was purified by treatment with oleum, washing with water, drying (CaCl_2), and distillation. The gas chromatograph was a Carle Model 9500 equipped with a flame ionization detector and $6 \text{ ft} \times \frac{1}{8}$ in. stainless steel columns packed with 10% SF-96 on 60-80 Chromosorb W. Analyses were run at least in duplicate on duplicate reaction samples; quantitation was by the internal standard method, using a Spectra-Physics "Minigrator" for peak integration. Fluorescence spectra were run in aerated isooctane (or other) solution at 23 °C, using a Perkin-Elmer Hitachi Model MPF-2A recording spectrofluorimeter. Fluorescence quenching constants were obtained by the Stern-Volmer method; the solutions were prepared as follows. Aliquots (1 mL) of a stock solution (1.0×10^{-2} M) of the naphthalene compound were placed in each of seven 10-mL volumetric flasks, to which were added 0.0-, 0.0-, 0.5-, 1.0-, 2.0-, 3.0-, and 5.0-mL aliquots of an appropriately concentrated stock solution of the quencher. The flasks were then filled to the mark with solvent. Gas chromatography in conjunction with mass spectrometry (GC/MS) was run on a VG 7070-F instrument operated by Mr. H. S. McKinnon, to whom we express our thanks. Photolyses were carried out in quartz ampoules, which were sealed to Pyrex standard taper joints by means of a graded seal for evacuation by the freeze-pump-thaw method. The light source was a Rayonet Model RPR photoreactor equipped with RPR 2537 lamps (maximum output 254 nm). Experiments were carried out at least in duplicate, using a "merry-go-round" to ensure equal light absorption by the ampoules. Ferrioxalate actinometry was used to monitor the light absorption.¹⁴

(13) For discussion, see ref 7.

(14) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1966, p 783.

Table IV. TFA Quenching of the Fluorescence of Benzene Derivatives

substituents	$k_q\tau$, M^{-1}	τ , ¹⁵ ns	k_q , $\text{M}^{-1} \text{s}^{-1}$
none	18	33.6	5.3×10^8
CH_3	26	35.2	7.3
C_2H_5	14	35.1	3.9
<i>n</i> - C_3H_7	15	36.0	4.1
<i>i</i> - C_3H_7	25	36.0	10.2
<i>n</i> - C_4H_9	21	29.2	7.1
<i>i</i> - C_4H_9	16	33.3	4.8

Table V. Quantum Yield of Hydrogen Exchange in $\text{C}_{10}\text{H}_8/\text{CF}_3\text{CO}_2\text{D}$

$[\text{CF}_3\text{CO}_2\text{D}]$, M	$\phi_{\text{ex}} \times 10^3$	
	run 1	run 2
0.10	6.2	6.7
0.20	7.6	9.0
0.30	7.9	9.7
0.40		12.9

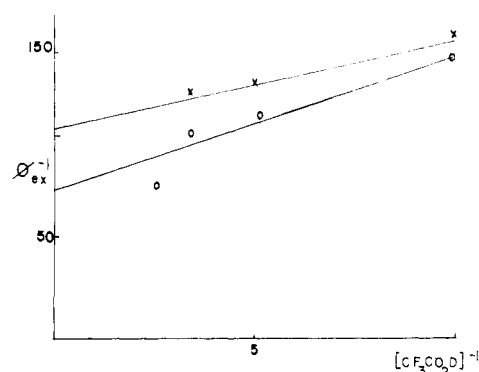


Figure 1. Plot of ϕ_{ex}^{-1} vs. $[\text{CF}_3\text{CO}_2\text{D}]^{-1}$ for the reaction $\text{C}_{10}\text{H}_8 + \text{CF}_3\text{CO}_2\text{D} \xrightarrow{h\nu} \text{C}_{10}\text{H}_7\text{D} + \text{CF}_3\text{CO}_2\text{H}$.

Irradiation of 4,4'-Dichlorobiphenyl with $\text{CF}_3\text{CO}_2\text{D}$. Duplicate solutions (2.0 mL) of 4,4'-dichlorobiphenyl (5.0×10^{-3} M) and $\text{CF}_3\text{CO}_2\text{D}$ (0.2 M) in ether were irradiated for 14 h. Analysis of the photolyzed solutions by GC/MS showed the following peak ratios: biphenyl *m/e* 155:154, irradiated sample 22.5:100, control sample 13.2:100; 4-chlorobiphenyl *m/e* 189:188, irradiated sample 20.8:100, control sample 13.9:100; 4,4'-dichlorobiphenyl *m/e* 223:222, irradiated sample 16.9:100, control sample 13.9:100.

In a separate experiment, 4,4'-dichlorobiphenyl was irradiated with $\text{CF}_3\text{CO}_2\text{H}$ at the same reagent concentrations. After 14 h, the extent of reaction was 68%; in control experiments where the $\text{CF}_3\text{CO}_2\text{H}$ was omitted, only 36% reaction occurred.

Attempted Sensitization of the Naphthalene- $\text{CF}_3\text{CO}_2\text{D}$ Reaction with Benzophenone. The solutions contained naphthalene (5.0×10^{-3} M) and $\text{CF}_3\text{CO}_2\text{D}$ (0.2 M), with or without benzophenone (5.0×10^{-2} M). At 254 nm, 97% of the light was absorbed by benzophenone. Analysis by GC/MS showed the relative abundance of *m/e* 129:128 in the mass spectrum to be 0.128, 0.126, and 0.120 in the sensitized, unsensitized, and unirradiated samples, respectively.

Fluorescence Quenching of Aromatics by TFA and Other Acids. The method is described above. In addition to the results in Table II, a series of substituted benzenes was studied (Table IV).¹⁵

Hydrogen Exchange with Naphthalene- $\text{CF}_3\text{CO}_2\text{D}$. The reactants were naphthalene (5.0×10^{-3} M) and concentrations of $\text{CF}_3\text{CO}_2\text{D}$ up to 0.4 M in isooctane. These were irradiated in duplicate for 24 h. The photolysate was analyzed by GC/MS, the ratio of *m/e* 129 to *m/e* 128 being studied. GLC indicated that over this time period, some of the naphthalene was irradiated to destruction. In addition, the *m/e* 129:128 ratio had to be corrected for the ^{13}C natural abundance and for exchange in the dark controls. The quantum yields were not as reproducible from

(15) P. M. Froehlich and H. A. Morrison, *J. Phys. Chem.*, **76**, 3566 (1972).

run to run as would be desired (see Table V). The data are plotted in Figure 1. The slopes and intercepts are in good agreement, considering the experimental problems.

Hydrogen Exchange with *p*-Dodecylbenzenesulfonic Acid. The sulfonic acid, obtained from Pilot Chemical Co., was purified by chromatography over alumina. The Stern-Volmer quenching constant for quenching naphthalene fluorescence was 22 M^{-1} in isooctane. Hydrogen exchange was studied in the system C_{10}D_8 /*p*-dodecylbenzenesulfonic acid. The hydrocarbon ($6.0 \times 10^{-3} \text{ M}$) and the acid (0.20 M) were irradiated together for 18 h. GC/MS analysis of the photolysate indicated that the quantum yield of hydrogen exchange ($\text{C}_{10}\text{D}_8 \rightarrow \text{C}_{10}\text{D}_7\text{H}$) was 0.05.

Reaction of 1-Chloronaphthalene with TFA in Ether. The solutions contained $5.0 \times 10^{-3} \text{ M}$ 1-chloronaphthalene and 0.2 M $\text{CF}_3\text{CO}_2\text{H}$ in dry ether. After 14-h irradiations, the extent of reaction was 90%, while control samples without TFA had reacted to the extent of 56%. A similar experiment using $\text{CF}_3\text{CO}_2\text{D}$ in place of $\text{CF}_3\text{CO}_2\text{H}$ was analyzed by GC/MS. The ratio of *m/e* 163 to *m/e* 162 in the irradiated samples was 0.130, compared with 0.110 for the unirradiated 1-chloronaphthalene. For the naphthalene produced the ratio of *m/e* 129 to *m/e* 128 was 0.150, compared with 0.110 for an authentic compound.

Attempted Sensitization of TFA-Assisted Dechlorination of 1-Chloronaphthalene by *m*-Methoxyacetophenone. Solutions containing 1-chloronaphthalene ($5.0 \times 10^{-3} \text{ M}$) and TFA (0.2 M) were prepared with and without *m*-methoxyacetophenone (0.05 M). After 2.5 h of irradiation, the solutions were analyzed by GLC. The percent decomposition was 15% for the samples without added "sensitizer" and 2.8% in the sensitized samples. The percent light absorbed by *m*-methoxyacetophenone was 95%.

TFA-Assisted Reaction of 1-Chloronaphthalene in Solvents Other Than Ether. Concentrations of 1-chloro-

naphthalene and of TFA were $5.0 \times 10^{-3} \text{ M}$ and 0.2 M, respectively. The percent decomposition was compared for each solvent in the presence and absence of TFA after 3-h irradiation. For cyclohexane, the present reaction was not influenced by adding TFA; in the case of tetrachloroethylene as solvent, the percent reaction was 74 and 51% with and without TFA. When 1-octene was the solvent, the percent reaction was typically 16% without TFA and 17% with TFA, though it was variable from run to run.

Dechlorination of 1-Chloronaphthalene in the Presence of *p*-Dodecylbenzenesulfonic Acid. The solutions contained 1-chloronaphthalene ($5.0 \times 10^{-3} \text{ M}$) and the acid (0.2 M). After 2.5-h irradiation, percent reactions were 11 and 50% in the absence and in the presence of the acid.

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Registry No. Naphthalene, 91-20-3; 1-fluoronaphthalene, 321-38-0; 1-chloronaphthalene, 90-13-1; biphenyl, 92-52-4; 4,4'-dichlorobiphenyl, 2050-68-2; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; 2-fluoronaphthalene, 323-09-1; 2-chloronaphthalene, 91-58-7; 1-methoxynaphthalene, 2216-69-5; 2-methoxynaphthalene, 93-04-9; isooctane, 540-84-1; benzene, 71-43-2; 1-octene, 111-66-0; tetrachloroethylene, 127-18-4; acetonitrile, 75-05-8; dioxane, 123-91-1; ether, 60-29-7; ethanol, 64-17-5; methylbenzene, 108-88-3; ethylbenzene, 100-41-4; propylbenzene, 103-65-1; isopropylbenzene, 98-82-8; butylbenzene, 104-51-8; isobutylbenzene, 538-93-2; $\text{CF}_3\text{CO}_2\text{D}$, 599-00-8; 4-chlorobiphenyl, 2051-62-9; $\text{CF}_3\text{CO}_2\text{H}$, 76-05-1; benzophenone, 119-61-9; *p*-dodecylbenzenesulfonic acid, 121-65-3; C_{10}D_8 , 1146-65-2; $\text{C}_{10}\text{D}_7\text{H}$, 887-68-3; *m*-methoxyacetophenone, 586-37-8; cyclohexane, 110-82-7.

Alkyl Cation Formation and Hydride Transfer in the $\text{AlBr}_3/\text{SO}_2\text{FCl}$ System

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Until now the primary acidic systems which have been reported to be able to stabilize high concentrations of alkyl cations contain antimony pentafluoride. The ions have been detected and characterized principally by nuclear magnetic resonance spectroscopy. This report deals with an aluminum bromide system that can also stabilize high concentrations of tertiary alkyl cations. The NMR spectra of solutions of C_4 thru C_7 alkyl halides in $\text{AlBr}_3/\text{SO}_2\text{FCl}$ are the same as those found with SbF_5 in many solvents. The cations exhibit ^1H NMR shifts which are a function of the RX/AlBr_3 ratio and AlBr_3 concentration. Limiting shifts are found in 2 M solutions with ratios below 0.2. Regardless of the isomeric halide dissolved in the acid, the initial ions appear to isomerize rapidly to the most favored structures which are then observed. Thus the *tert*-butyl and *tert*-amyl ions are formed from butyl and amyl halides. The C_6 and C_7 systems yield a mixture of tertiary cations. The ions in $\text{AlBr}_3/\text{SO}_2\text{FCl}$ undergo extremely rapid hydride transfer reactions with hydride donors. The acid system is partially miscible with hydrocarbons and two-phase systems can easily be developed in which rapid transfer occurs in both phases.

At about the same time, two groups of investigators reported the detection by NMR spectroscopy of stable alkyl cations in systems containing antimony pentafluoride.¹ Whether the species being observed were truly stable ions or ions participating in rapid equilibrating processes was not established, but the spectral results were so striking as to make it likely that if an averaging process were involved, ions were heavy contributors.

The ^1H NMR spectra of solutions of alkyl halides in the SbF_5 containing systems are unique in that absorptions

are obtained significantly downfield of those in the parent compounds. In addition, first-order patterns are generally observed which could be rationalized with a model for the appropriate cation. One does not know a priori where the resonance of a stable cation would be, but the effects of charge and rehybridization of an sp^3 center to sp^2 should both result in downfield shifts of neighboring groups.

A wealth of information concerning cation behavior has developed from these studies. The initial systems included SbF_5 neat,² $\text{SbF}_5 + \text{HF}$,^{1b} $\text{SbF}_5 + \text{SO}_2$,¹ $\text{SbF}_5 + \text{HSO}_3\text{F}$,³

(1) (a) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963); (b) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc., London*, 147 (1964).

(2) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(3) G. A. Olah, and J. Lukas, *J. Am. Chem. Soc.*, **89**, 2227 (1967).