

(90%): NMR (CCl₄) δ 7.00 (2 H, AB pattern, $J = 7$ Hz), 4.41 (1 H, triplet, $J = 7$ Hz), 2.62 (2 H, m), 2.35 (3 H, s), 2.30 (3 H, s), 1.67 (4 H, m); IR (film) 1695 cm⁻¹. Anal. Calcd for C₁₃H₁₅ClO: C, 70.11; H, 6.79. Found: C, 70.02; H, 6.87.

Irradiation of 2-chloro-6,9-dimethylbenzuberone (7) was carried out with a 0.33-g sample (1.5 mmol) in 300 mL of methanol and irradiated under N₂ for 8 h with a Pyrex-filtered medium-pressure Hanovia lamp. The solvent was evaporated, and the residue was analyzed by GLC (170 °C, SE 30). One of the peaks was too small to be successfully analyzed. The four that were determined along with yields and spectral data are as follows:

2-Methoxy-6,9-dimethylbenzuberone (8): 6% yield; NMR (300 Hz, CDCl₃) δ 1.69 (2 H, m), 1.90 (2 H, m), 2.16 (3 H, s), 2.23 (3 H, s), 2.61 (2 H, m), 2.90 (3 H, s), 4.70 (2 H, d of d, $J = 1.4$ and 3.0 Hz), 6.98 (2 H, s). The multiplets above include appropriate splitting for cis, trans, and geminal coupling: $J = 1.4, 3.0,$ and 15.0 Hz; $m/e = 218$ (21, M⁺), 190 (18, M - CO), 186 (45, M - CH₃OH), 175 (33, M - CO - CH₃); IR (film) 1695 cm⁻¹. Anal. Calcd for C₁₄H₁₈O₂: C, 77.03; H, 8.31. Found: C, 77.05; H, 8.20.

5-Carbomethoxy-1,4-dimethyltetralin (5c): 34% yield; NMR (CDCl₃, 300 Mz) δ 1.81 (4 H, m), 2.09 (3 H, s), 2.17 (3 H, s), 2.51 (2 H, m), 2.70 (1 H, d of d), 3.62 (3 H, s), 6.78 (1 H, d), 6.84 (1 H, d); $m/e = 218$ (20, M⁺), 159 (100, M - CO₂Me); IR (film) 1740 cm⁻¹. Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.32; H, 7.82.

α -Chloropropiophenone: 68% yield; bp 160-162 °C (16 torr); IR (neat) 1695 cm⁻¹; NMR (CCl₄) δ 1.70 (3 H, d), 5.11 (1 H, q), 7.47 (3 H, m), 7.96 (2 H, m).

Irradiation of α -Chloropropiophenone. A 1.0-g sample was dissolved in 400 mL of methanol and irradiated with a Pyrex-filtered Hanovia lamp for 15 h. Evaporation of methanol, solution in hexane, extraction with aqueous bicarbonate solution, and drying (MgSO₄) afforded crude material that was separated by preparative gas chromatography. Two major products were obtained: propiophenone, identified through identity of IR and NMR spectra and methyl α -phenylpropionate (**5e**), identified from spectra properties: IR 1735 cm⁻¹; NMR (CCl₄) δ 1.37 (3 H, d) 3.66 (3 H, s) 3.70 (1 H, q) 7.27 (5 H, m). Up to 20 mol % water causes no change in product distribution.

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Registry No. **1a**, 88632-72-8; **1b**, 50690-11-4; **1d**, 50690-12-5; **2a**, 66309-83-9; **2b**, 24623-20-9; **2d**, 6682-69-5; **3a**, 99356-69-1; **3b**, 66521-22-0; **3c**, 16198-27-9; **4a**, 35031-52-8; **4c**, 99356-71-5; **4d**, 1667-01-2; **5a**, 99356-70-4; **5c**, 99356-68-0; **5d**, 41841-19-4; **5e**, 31508-44-8; **6**, 99356-65-7; **7**, 99356-66-8; **8**, 99356-67-9; **10**, 99376-43-9; *p*-C₆H₄(CH₃)₂, 106-42-3; ClCH₂COCl, 79-04-9; C₆H₅COCHClCH₃, 6084-17-9; C₆H₅COCH₂CH₃, 93-55-0.

Reaction of Fluoroxytrifluoromethane with Ring-Substituted Styrenes: A Structure-Reactivity Study

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The reaction of fluoroxytrifluoromethane (FTM) with a group of ring-substituted styrenes has been studied. Reaction products have been determined, and relative rates for addition to the double bond have been measured by a competition method. The data give a straight line when plotted as log (k/k_H) vs. Hammett σ values with a ρ of -2.48. A similar plot vs. σ^+ gave less satisfactory agreement with linearity and a ρ of -2.18. A mechanism is proposed in which a spin-paired free-radical pair is formed that is converted by electron transfer into an ion pair.

Despite the high electronegativity of fluorine, there are some reagents that, in their reactions with organic compounds in solution, appear to behave as sources of the fluorine cation. These include fluorine,^{2a} oxygen difluoride,^{2c} fluoroxytrifluoromethane (FTM),³ and fluoroxypentafluoroethane.⁴ The reagent for which the most extensive experiments have been performed is fluoroxytrifluoromethane (FTM), which has been used by Barton and his co-workers to introduce fluorine into organic compounds by reactions both with the carbon-carbon double bond and, to a lesser extent, with the carbon-hydrogen bond. The evidence that the FTM-alkene reactions studied by Barton et al. proceed by an electrophilic fluorination mechanism has been summarized by Hesse.³ A study of the reaction of FTM with ring-substituted styrenes has been carried out in this laboratory in order to examine quantitatively the reaction of FTM with a group of alkenes in which a greater range of polar nature exists than has been the case in previous studies. The results are reported below.

Results

In choosing an experimental method for this study an important consideration was the question of the supply of FTM. The reagent is expensive and, for a time, was commercially unavailable, necessitating its synthesis for use in some of the experiments. Accordingly, a procedure using large amounts of this reagent such as bubbling it through a solution was ruled out. Attempts at preparing stable solutions of FTM in inert solvents were unsuccessful and a competition method was finally chosen (cf. the similar situation for fluorine).⁵ This involved admitting gaseous FTM to a vigorously stirred solution of two styrenes in fluorotrichloromethane solvent. The amount of FTM was chosen so that the amounts of styrenes consumed would allow accurate measurement of C_0/C_f ($C =$ concentration) for each. These experiments allowed the determination of the nature of the reaction products and of the relative rate constants. The styrenes used were styrene and *p*-chloro-, *m*-chloro-, *p*-methyl-, *m*-nitro-, and *p*-methoxystyrene. For the last one, reaction product structures could be determined but rate data could not.

Nature of the Reaction Products. FTM-Styrene Reaction. The identification of the products of the re-

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Table I. Percent Product Yields

| subst | VI ^a (addn of CF ₃ O, F) | VII (addn of 2 F) | II-V (β -fluorostyrene plus adducts) ^b |
|----------------------------|--|-------------------------|--|
| <i>p</i> -OCH ₃ | 0 | 0 | 100 |
| <i>p</i> -CH ₃ | 43 | 26 | 31 |
| H | 31 | 31 | 38 |
| <i>p</i> -Cl | 30 | 30 | 41 |
| <i>m</i> -Cl | 24 | 32 | 44 |
| <i>m</i> -NO ₂ | 37 | 11 | 53 |

^aThe Roman numerals refer to the styrene products identified earlier and to the analogous products for the substituted styrenes. ^bIt is proposed below that IV and V are primarily products and their reaction with FTM yields II and III.

action of FTM with styrene (I) was based on mass spectral data obtained on the Finnigan GC mass spectrograph, ¹H and ¹⁹F NMR spectra, and an independent synthesis of two of the products. Gas chromatographic examination of the reaction products yielded six peaks, each of which was shown by GCMS to correspond to a single compound. Examination of the mass spectra led to the assignment of the following structures, named in the order in which they were eluted: 2,2-difluoro-1-(trifluoromethoxy)-1-phenylethane (II); 1,2,2-trifluoro-1-phenylethane (III); *cis*- and *trans*- β -fluorostyrene (IV and V); 2-fluoro-1-(trifluoromethoxy)-1-phenylethane (VI); 1,2-difluoro-1-phenylethane (VII).

It did not prove possible to separate the six products cleanly by preparative gas chromatography. It was clear, however, that if styrene and the β -fluorostyrenes could be eliminated, the remaining products could be separated in this way. Accordingly, a reaction between styrene and excess FTM was carried out that yielded a product mixture containing no styrene or β -fluorostyrenes, i.e., only products II, III, VI, and VII above. This mixture was separated into the four components by preparative gas chromatography, and the ¹H and ¹⁹F spectra of these products were taken. These results gave strong support to the structures proposed.

The mixture of *cis*- and *trans*- β -fluorostyrene was then synthesized independently, and the synthetic mixture was shown by GCMS to be identical with the products IV and V of the FTM-styrene reaction. Treatment of these β -fluorostyrenes with FTM under reaction conditions yielded products II and III, as shown by GCMS.

The structures of the reaction products of the ring-substituted styrenes were assigned on the basis of GCMS analysis alone. The mass spectra of the products found for the styrene derivatives showed strong similarities to those found for the products from styrene so that the assignments have been made with considerable confidence. Of the products listed above for styrene, the analogue of each was observed in the products of the reaction of FTM with the ring-substituted styrenes with the exception of *p*-methoxystyrene. Here, only the *p*-methoxy- β -fluorostyrenes plus the analogues of products II and III, i.e., the fluorine and FTM adducts of the β -fluorostyrenes, were found. Estimates of product yields were made by comparing peak areas, i.e., by assuming that all the compounds had the same sensitivity to the flame ionization detector. Since, for similar compounds, such sensitivities do not vary by more than a few percent,⁶ the product yields, which are reported in Table I, are assigned a probable error of $\pm 5\%$.

Determination of Relative Rate Constants. In these experiments two styrenes were allowed to compete for a

Table II. Rate Data

| subst | no. of runs | k/k_H^a | matl bal ^b |
|--|-------------|-------------------|-----------------------|
| <i>p</i> -Cl | 3 | 0.47 \pm 0.01 | 1.04 \pm 0.04 |
| <i>m</i> -Cl | 5 | 0.16 \pm 0.01 | 0.90 \pm 0.20 |
| <i>p</i> -CH ₃ | 2 | 3.1 \pm 0.3 | 1.08 \pm 0.08 |
| <i>m</i> -NO ₂ ^c | 5 | 0.021 \pm 0.003 | 1.00 \pm 0.16 |

^aUncertainties are given in terms of standard deviation from the mean. ^bMoles of styrene consumed/moles of FTM used. ^cThe value measured was $k_{m\text{-NO}_2}/k_{m\text{-Cl}} = 0.14 \pm 0.04$, and this has been converted to $k_{m\text{-NO}_2}/k_H$ by multiplying by $k_{m\text{-Cl}}/k_H$.

limited amount of FTM. The experimental measurements consisted of determining the peak areas of the two styrenes before and after reaction as well as the peak area of toluene, which served as an internal standard. Relative rate constants were given by

$$k_A/k_B = \ln(A_0/A_f)_A / \ln(A_0/A_f)_B$$

where A_0 and A_f are the peak areas at the beginning of reaction and at the end, normalized for the toluene peak area. As has been pointed out,⁷ the only requirement for the competition method is that the competing processes be of the same kinetic order. For the expression above the order in the styrenes is taken as 1. No problems were encountered in competition experiments involving the pairs: styrene-*p*-chlorostyrene and styrene-*m*-chlorostyrene. The reactivity of *m*-nitrostyrene proved too low to allow accurate results to be obtained by its competition with styrene. Instead, it proved satisfactory to make measurements on the *m*-nitrostyrene-*m*-chlorostyrene pair. For *p*-methylstyrene initial experiments in which more alkene was consumed than FTM added suggested that polymerization was competing with the FTM reaction. When the experiments were carried out at concentrations one-fifth as great as those used initially, this difficulty was eliminated. For *p*-methoxystyrene it was found that not only was the reaction rate too high for accurate measurement by competition with styrene but also, as in *p*-methylstyrene, polymerization was apparently occurring. It did not help to use more dilute solutions here, and as a consequence no kinetic data were found for this species. In a study of the addition of 2,4-dinitrobenzenesulfonyl chloride to *p*-methoxystyrene⁸ anomalously high reaction rates were also reported, and the fact that similar behavior has been observed in the ionic polymerization of *p*-methoxystyrene⁹ was noted.

In these experiments a material balance has been determined in the form of moles of styrenes consumed per mole of FTM and is shown in Table II. Given the uncertainty in the analysis mentioned above in the discussion of Table I, we believe that the results support the proposal that the products reported represent the course the reaction takes.

Treatment of the Data. The logarithms of the rate constants relative to unsubstituted styrene [$\log(k/k_H)$] have been plotted vs. the Hammett σ and Brown-Okamoto σ^+ substituent constants. The values used are as follows:¹⁰ *p*-Cl, $\sigma = 0.23$, $\sigma^+ = 0.11$; *m*-Cl, $\sigma = 0.37$, $\sigma^+ = 0.40$; *p*-CH₃, $\sigma = -0.17$, $\sigma^+ = -0.31$; *m*-NO₂, $\sigma = 0.71$, $\sigma^+ = 0.67$.

Figure 1 shows the ρ - σ plot. The ρ value was obtained by the method of least squares and found to be -2.48 ± 0.09 with a correlation coefficient of 0.990. The ρ obtained

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Table III. Compilation of Values for Some Representative Reactions

| reaction | ρ | subst const used | ref |
|--|---------------|-------------------------|--------------|
| acid-catalyzed hydr of styrenes | -3.58 | σ^+ | 21 |
| acid-catalyzed hydr of α -methylstyrenes | -3.21 | σ^+ | 22 |
| addn of 2,4-dinitrobenzenesulfonyl chloride to styrene | -2.40 | σ | 6 |
| bromin of styrenes | -4.5 | σ^+ | 23 |
| chlorin of styrene | -3.22 | σ^+ | 24 |
| addn of FTM to styrene | -2.48 | σ | present work |
| | -2.14 | σ^+ | |
| ionic polymerizn of styrene | -1.70 (-2.21) | σ (σ^+) | 7 |
| free-radical polymerizn of styrene | +0.509 | σ | 25 |
| free-radical side-chain chlorin of toluene | -0.66 | σ^+ | 26 |
| free-radical side-chain bromin of toluene | -1.36 | σ^+ | 27 |
| addn of toluene- <i>p</i> -sulfonyl free radicals to styrene | -0.50 | σ^+ | 28 |
| | -0.55 | σ | 28 |

from the plot of the data using σ^+ constants gave a ρ of -2.18 ± 0.06 with a correlation coefficient of 0.983. Both coefficients are significantly better than the value of 0.95, suggested by Jaffe¹¹ as a satisfactory index of linearity.

Discussion

Before interpreting the present results, it is useful to describe the status of knowledge of the reaction of FTM with alkenes. The first such reaction was carried out by Porter and Cady.¹² It involved the gas-phase addition of FTM to perfluorocyclopentene at 80 °C, presumably by a free-radical chain reaction. (The kinetics and mechanism of the FTM-hexafluoropropene reaction have recently¹³ been studied, and evidence for a free radical chain mechanism has been found.) About 10 years later the reaction of FTM with steroidal alkenes was studied by Barton and co-workers¹⁴ as a means of introducing fluorine into steroids. The first alkene studied was 3-acetoxy-5- α -cholest-2-ene. The results were interpreted in terms of donation of a fluorine cation to the alkene. The principal pieces of evidence developed in this and later papers adduced for the polar mechanism were as follows: (a) the direction of addition, which was consistent with a polar but not a free-radical chain mechanism;¹⁵ (b) the occurrence of a rearrangement characteristic of carbocations in a suitably constituted substrate;¹⁶ (c) incorporation of the solvent methanol in the adduct obtained from the reaction of FTM with stilbene;¹⁷ (d) the absence of any effect of oxygen, toluene, or other species that would be expected to affect radical chain reactions.¹⁸ Another point that emerged from the FTM-stilbene studies was the preponderance of cis addition in the reaction. Barton¹⁸ has proposed that predominant cis addition is characteristic of electrophilic addition to alkenes when an intermediate cyclic ion is not formed. Dolbier¹⁹ has made similar arguments, proposing that such stereochemistry arises from collapse of a π complex in which the reagent bridges the double bond. Merritt²⁰ has also presented such a picture. The stereochemistry has thus also been considered as consistent with a polar mechanism.

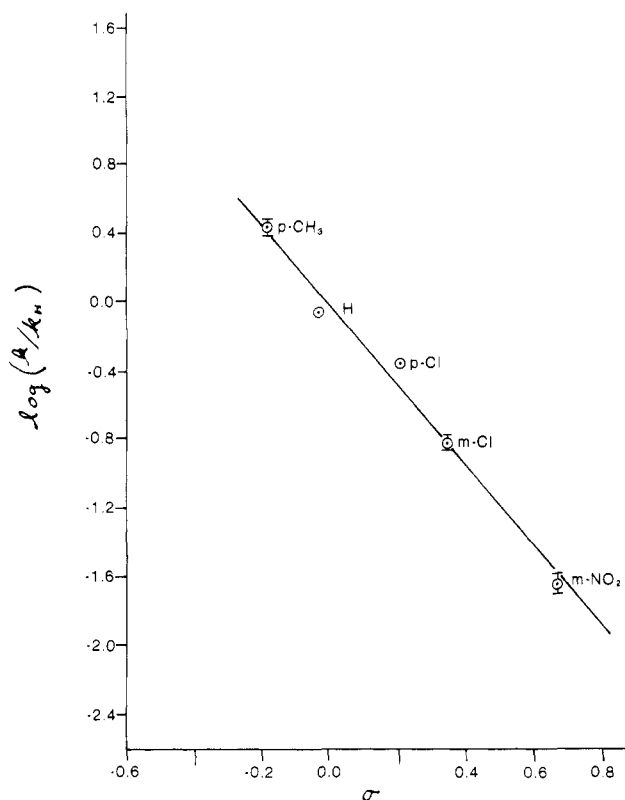


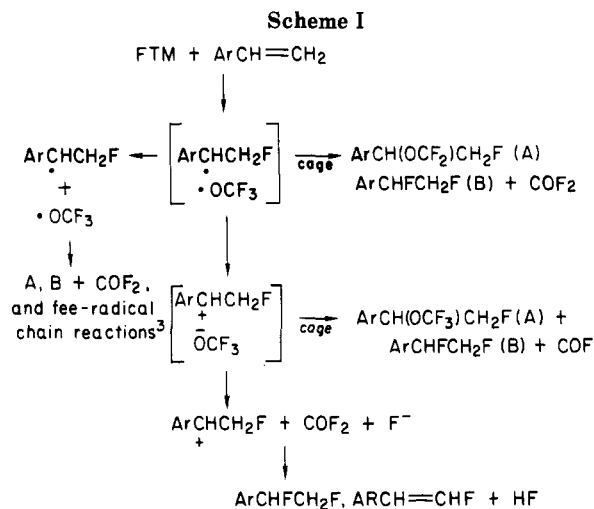
Figure 1. ρ - σ plot for FTM addition to ring-substituted styrenes: ordinate, $\log(k/k_H)$; abscissa, σ .

On the other hand, Johri and DesMarteau²⁰ have concluded from a comparison of the reaction of FTM and chloroxytrifluoromethane (CTM) with a number of simple alkenes that while the results with CTM were consistent with a polar mechanism, those with FTM were more consistent with a homolytic mechanism.

Results of the Present Work. The results of the present work that we feel need to be explained are as follows: (a) the nature of the reaction products, including

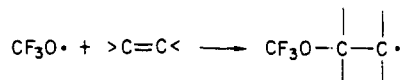
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the somewhat anomalous results with *p*-methoxystyrene; (b) the magnitude of the ρ found.

We feel that our results exclude a free-radical chain reaction, e.g.:



The ρ values found, -2.48 (σ) and -2.18 (σ^+), are consistent with cationic intermediates rather than with the attack of a free radical on the alkene bond. The latter reactions can show polar effects but they give much smaller ρ values than that found here. This is shown by the data of Table III where ρ values for pertinent free-radical and polar reactions are collected. One may note, indeed, that the ρ value found here fits in well with those reported for the addition of chlorine and bromine to styrenes. (We offer below, however, a different explanation for the magnitude of this ρ .) The reaction products found can likewise be explained through reactions of β -fluoro- α -arylethyl cations, analogous to those written by Patrick et al.²⁹ for the reaction of FTM with 1,1-diphenylethylene. (See below.)

We address, however, a central problem of the mechanism in which FTM donates a fluorine cation to an alkene, i.e. the fact that the structure of FTM does not make such a transfer likely. An accompanying aspect of this problem is that the comparative weakness of the oxygen-fluorine bond in FTM, $44.7 \text{ kcal mol}^{-1}$,³⁰ makes the formation of free-radical species quite reasonable.

The structure of FTM has been examined by electron diffraction,³¹ electron impact,³² microwave spectroscopy,³³ and by ab initio molecular orbital calculations.³⁴ The molecule has a small, $\sim 0.30 \text{ D}$, dipole moment,³³ the oxygen-fluorine bond is not very polar,³⁴ and the fluorine end of the bond is the more negative.³² One can adduce further support for the lack of ionic nature of the oxygen-fluorine bond from the fact that the bond strength, $44.7 \text{ kcal mol}^{-1}$,³⁰ is close to that calculated as the average of the fluorine-fluorine bond and the oxygen-oxygen bond in bis(trifluoromethyl) peroxide.³⁵ The values are $\text{F}-\text{F} = 37.8$ ³⁶ kcal mol^{-1} and $\text{CF}_3\text{O}-\text{OCF}_3 = 46.7$ ³⁰ kcal mol^{-1} , to

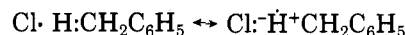
yield an average of $42.2 \text{ kcal mol}^{-1}$.

We propose that the FTM-alkene reactions occur through the initial formation, in a solvent cage, of a spin-paired radical pair that can undergo various reactions. The mechanism is given in Scheme I. The spin-paired radical pair is shown undergoing (a) cage reactions to give the adducts of FTM, A, and the difluoride, B, (b) diffusion out of the cage with subsequent reactions of the free radicals to give products A and B and chain initiation, and (c) electron transfer to give an ion pair. The ion pair is shown to react in the cage to give products A and B and to diffuse out of the cage. The trifluoromethoxide ion, which, Hesse³ has pointed out, is very unstable, decomposes to carbonyl fluoride and fluoride ion. The latter then reacts with the cation to generate the β -fluorostyrenes. For our system diffusion of the radicals out of the cage, which could lead to free-radical chain reactions, is assumed to represent a very small contribution, since such chain reactions would yield different products than those observed.

We offer the following arguments for this scheme:³⁷ (1) The initial reaction of FTM and the alkene is one for which there is good evidence in the gas phase.¹³ (2) Good evidence for electron transfer of the kind shown has been presented for the reaction of neopentyl radical and *m*-chlorobenzoate radical³⁹ and for the reaction of the 1-norbornyl radical with iodide atom.⁴⁰ It has been suggested³⁹ that electron transfer is a general reaction for two radicals with "much different electronegativities". (3) The fact that activated alkenes (i.e., those bearing groups like methoxyl and amino) react more cleanly with FTM than do unactivated ones¹⁸ may be explained by the idea that diffusion out of the cage by radicals and subsequent reaction competes more favorably with ion-pair formation for unactivated than for activated alkenes and that radical fragmentation leads to a more complex product mixture.

The formation of β -fluorostyrenes is shown above as occurring outside the cage. This has been done to explain the fact that the only products found for the *p*-methoxystyrene-FTM reaction were those proceeding through β -fluoro-*p*-methoxystyrene. The *p*-methoxystyrene-FTM reaction would yield the most stable carbocation of our series and hence the one for which diffusion out of the cage would compete most successfully with combination in the cage.

It remains to consider the magnitude of the ρ value that, it has been pointed out, is more characteristic of ionic than free-radical intermediates, whether the value found for the σ correlation or that found for the σ^+ correlation is used. The polar effects in the radical reactions shown in Table III are explained, using the chlorine atom-toluene reaction as an example, by resonance structure of the following sort:⁴¹



As Table III shows, such reactions are characterized by ρ values that are small compared to that found here. For a transition state in which a spin-paired radical pair is in

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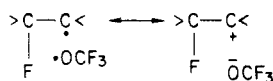
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the process of formation, the situation is somewhat different:



In the chlorine atom-toluene case the charged form is written with one less covalent bond while in the above situation this is not the case. A greater contribution of the charged form is thus reasonable. Similar resonance forms have been written to explain effects of differing electro-negativities in a radical pair on their combination rate,⁴² for radical pairs formed in diacyl peroxide decomposition,³⁸ and to explain the effect of neighboring iodide and sulfide groups in *tert*-butyl perester decompositions.⁴³ It thus seems reasonable that, for a system of the sort proposed here, larger values of ρ can make sense than is the case for systems involving a single radical.

One consequence of the above proposal is that carrying these reactions out in a solvent may lead to results different from those in the gas phase, independent of questions of solvent polarity. If a radical pair is formed by a reaction in solution, the members are forced to undergo many collisions before they diffuse apart, and this may have consequences if electron transfer can occur. In the gas phase the number of collisions occurring between members of the radical pair before they diffuse apart will be much smaller and the opportunities for electron transfer to give ions will be thus much less.

Experimental Section

Reagents. The following compounds were obtained from Pfaltz and Bauer, Inc. and were distilled before use: styrene (bp 145–146 °C), *p*-methylstyrene (bp 170–171 °C), *p*-chlorostyrene (bp 192 °C); *m*-chlorostyrene (bp 62–83 °C (6 torr)), *m*-nitrostyrene (bp 90–96 °C (3.5 torr)). Other chemicals were obtained from the following suppliers: fluoroxyltrifluoromethane and carbonyl fluoride, PCR Research Chemicals; fluorine, Air Products; trichlorofluoromethane, Matheson Co. All solvents and materials were reagent grade.

General Methods. FTM was synthesized according to the procedure described by Kennedy and Cady⁴⁴ and stored in the metal cylinders in which the commercial product had been supplied. Completed reaction of carbonyl fluoride was demonstrated by IR analyses. The competition experiments were carried out in a Pyrex round-bottom flask mounted on a glass vacuum line and cooled by a dry ice-acetone bath (–78 °C). Pressures were measured by a Pace Model V7 pressure transducer. Products analyses were made on a Perkin-Elmer Sigma 3 gas chromatograph equipped with a 150-ft length \times 0.101-in. i.d. SE-52 capillary column. Preparative separations were performed on a Varian Model 2720 gas chromatograph using a 15% SE 12 ft \times 0.25 in. column. Infrared spectra were determined on a Beckman Model 5-A and on a Perkin-Elmer Model 297 spectrophotometer.

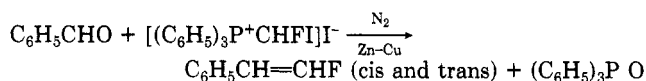
Procedure for a Competition Experiment. All of these experiments involved a binary mixture of styrenes. In a typical experiment, 1–1.5 mmol each of styrenes A and B and 1 mmol of toluene were weighed into a 25-mL round-bottom reaction flask. A few drops were withdrawn for analysis, and 10 mL of fluorotrichloromethane was added. A Teflon-coated stirring bar was placed in the flask, and the flask was attached by a ground joint to the vacuum line. It was cooled in a dry ice-acetone bath for 15 min and evacuated and 1.2 mmol of gaseous FTM admitted to the vigorously stirred solution, which was then closed off by

a stopcock (lubricated with Fluorolube). After 15 min of stirring the flask was removed from the manifold, carbon tetrachloride (1 mL) added, and the fluorotrichloromethane distilled away. The sample taken before reaction and the final mixture were subjected to GC analysis.

Product Separation and Characterization for the FTM-Styrene Reaction. Styrene (0.208 g, 2.0 mmol) was allowed to react with FTM (4 mmol), according to the procedure described above. Carbon tetrachloride (1 mL) was added, and the excess fluorotrichloromethane was removed by fractional distillation. Products II, III, VI, and VII were separated on a 15% SE-52 column (12 ft \times 1/4 in.) at an oven temperature of 120 °C. Samples were collected in GC collection tubes containing a few drops of carbon tetrachloride chilled in a dry-ice-2-propanol bath.

Mass spectrographic analysis were made on the Finnigan GC mass spectrograph, and ¹H and ¹⁹F NMR spectra were run on a Bruker WH 90 (Fourier transform) NMR spectrometer. Tetramethylsilane was the internal standard for the ¹H spectra, and fluorotrichloromethane was the internal standard for the ¹⁹F spectra.

Synthesis of Cis and Trans Mixture of β -Fluorostyrenes. The mixture of *cis*- and *trans*- β -fluorostyrenes was prepared by the method of LeGoff⁴⁵ by the reaction, under nitrogen, of benzaldehyde and (fluoriodomethyl)triphenylphosphonium iodide:



The product was analyzed on the GC mass spectrograph and shown to be identical with products IV and V of the FTM-styrene reaction.

Spectral Data For FTM-Styrene Products. $C_6H_5CH^1-(OCF_3)CH^2F_2$: mass spectrum, *m/e* 175 ($C_6H_5C^+HO CF_3$), 109 ($C_7H_6F^+$), 69 (CF_3^+), 141 ($C_6H_5C^+HCH F_2$), 226 (molecular ion); ¹⁹F NMR ($C_6H_5CH(OCF^A)CH^B F_2$) Ph_A 58.3 (s), Ph_B 126.7 (t or d of d), $J_{F^A-H^1} = 9.67$ Hz, $J_{F^B-H^2} = 59.5$ Hz; ¹H NMR, $\delta(H^1)$ 5.2 (td), $\delta(H^2)$ 5.9 (td).

$C_6H_5CH^1FCH^2F_2$: mass spectrum, *m/e* 109 ($C_7H_6F^+$), 160 (molecular ion), 83 ($CF_2HCH F^+$), 91 ($C_7H_7^+$), 122 ($C_6H_5CHCH F^+$); ¹⁹F NMR ($C_6H_5CH^1F^ACH^2F^B$) Ph_A 195.8 (dt), Ph_B 129.8 (tt or tdd), $J_{F^A-H^1} = 43.9$ Hz, $J_{F^B-H^1} = 12.2$ Hz, $J_{F^B-H^2} = 58.6$ Hz), ¹H NMR, $\delta(H^1)$ 5.5 (dm), $\delta(H^2)$ 6.2 (tm).

$C_6H_5CH=CHF$ (Cis and Trans): mass spectrum, *m/e* 122 (molecular ion), 121 ($C_6H_5C^+CHF$), 96 ($C_6H_5F^+$), 101 ($C_6H_5C\equiv C^+$), 102 ($C_6H_5\equiv CH^+$), ¹⁹F NMR ($C_6H_5CH^1=CH^2F^B$) Ph_{F^B} 122.94 (cis), 130.01 (trans), $J_{F^B-H^1} = 44.39$ Hz (cis), 19.42 Hz (trans), $J_{F^B-H^2} = 83.23$ Hz (cis), 82.0 Hz (trans).

$C_6H_5CH(OCF_3)CH_2F$: mass spectrum, *m/e* 127 ($C_6H_5C^+F_2$), 109 ($C_7H_6F^+$), 175 ($C_6H_5C^+HO CF_3$), 208 (molecular ion), 69 (CF_3^+), 123 ($C_6H_5C^+HCH_2F$), 105 ($C_6H_5C^+O$); ¹⁹F NMR ($C_6H_5CH^1-(OCF^A)CH_2^B F$) Ph_A 58.9 (s), Ph_B 221.0 (td), $J_{F^A-H^1} = 17.86$ Hz, $J_{F^B-H^2} = 47.64$ Hz; ¹H NMR, $\delta(H^1)$ 5.37 (m), $\delta(H_2)$ 6.2 (tm).

$C_6H_5CHFCH_2F$: mass spectrum, *m/e* 109 ($C_7H_6F^+$), 142 (molecular ion), 122 ($C_6H_5C=CHF^+$), 83 (CHF_2C^+HF) 91 ($C_7H_7^+$); ¹⁹F NMR ($C_6H_5CH^1F^ACH_2^B F$) Ph_A 187.2 (m), Ph_B 223.8 (tt), $J_{F^A-H^1} = 48.58$ Hz, $J_{F^A-H^2} = 16$ Hz, $J_{F^B-H^1} = 21$ Hz, $J_{F^B-H^2} = 48$ Hz, $J_{F^A-F^B} = 21$ Hz; ¹H NMR $\delta(H^1)$ 5.70 (qt), $\delta(H_2)$ 4.61 (qt).

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Registry No. I, 100-42-5; II, 99309-80-5; III, 99326-88-2; IV, 20405-78-1; V, 20405-77-0; VI, 99309-81-6; VII, 33315-79-6; FTM, 373-91-1; *p*-ClC₆H₄CH=CH₂, 1073-67-2; *m*-ClC₆H₄CH=CH₂, 2039-85-2; *p*-MeC₆H₄CH=CH₂, 622-97-9; *m*-NO₂C₆H₄CH=CH₂, 586-39-0; *p*-MeOC₆H₄CH=CH₂, 637-69-4; PhCHO, 100-52-7; Ph₃P⁺CHFI⁻, 55904-32-0.

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