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Photooxidation of 9-(Methoxymethylene)fluorene

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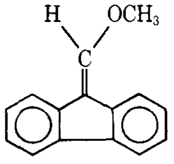
Abstract: The unsensitized photooxidation of 9-(methoxymethylene)fluorene (**1**) in carbon tetrachloride yields mixtures of epoxide (**2**) and fluorenone (**3**) in ratios from 0.04 at −20 °C to 2.6 at 75 °C. The efficiency of the oxidation depends on the chain character ($\phi = 12$) imparted by even small concentrations of carbon tetrachloride or tetrabromide. The reaction can be initiated thermally by generating the bromoperoxy radical **5** in the dark in the presence of **1** and oxygen. Mixtures of **1** and 2,3-dimethyl-2-butene show little change in the hydrocarbon without added sensitizer but rapid formation of allylic hydroperoxide when tetraphenylporphin is added. This evidence shows that singlet oxygen is not involved in the photooxidation of **1**. A chain mechanism is proposed.

Photooxidation of alkenes has been accomplished by (1) sensitized oxidation generating singlet oxygen[1] as the oxidizing agent; (2) self-sensitized oxidation[2] (probably involving singlet oxygen); and (3) sensitized oxidation, especially with α-diketones, not involving singlet oxygen.[3] Of particular interest has been the mechanism by which certain photooxidations[3,4] lead to epoxides as products. Recent reports of epoxides accompanying the reaction of singlet oxygen with biadamantylidene,[4c] norbornene,[4d] and binorbornylidene[4a,b] have been interpreted as indicating deoxygenation of intermediate peroxiranes by pinacolone[4c] or singlet oxygen[4b,e] (yielding ozone). Recent results in this laboratory[3,5] indicate that the photooxidation of alkenes to epoxides, sensitized by biacetyl or benzil, does not involve singlet oxygen. We now report unsensitized photooxidation of 9-(methoxymethylene)fluorene (**1**) to epoxide (**2**) and fluorenone (**3**) under conditions where singlet oxygen is not generated.



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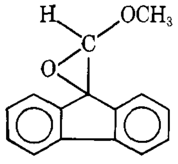

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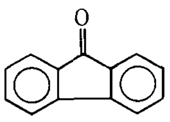
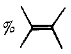
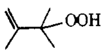


3

Results

Irradiation of 9-(methoxymethylene)fluorene (**1**) in carbon

Table I. Simultaneous Photooxidation[a] **1** and 2,3-Dimethyl-2-butene with and without Added Sensitizer. Tetraphenylporphin (TPP)

		Reaction mixture composition				
		From **1**			From 2,3-dimethyl-2-butene	
Sensitizer	Time, min	% **1**	% **2**	% **3**	% 	% 
None	15	45	35	(20)[b]	80	<5
TPP 8.5×10^{-4} M	5	70	12	(18)[b]	<5	93

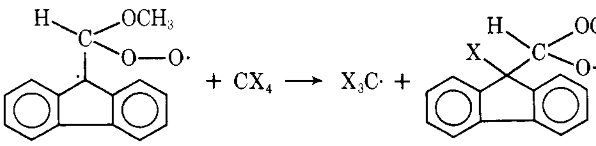
[a] Initial concentration of **1**, 0.096 M; of 2,3-dimethyl-2-butene, 0.095 M; all irradiations with a Sylvania 600-W projection lamp; solvent, CCl_4. [b] Reaction mixture composition was determined by integration of product and reactant methyl signals in the NMR spectra of the mixtures relative to bibenzyl as internal standard. Fluorenone, though not determined directly by this method, was the only other fluorene derivative obtained and could be estimated by difference in these experiments. For chromatographic isolation, see Experimental Section.

tetrachloride in the presence of oxygen with either a Rayonet 3500 Å lamp or a Sylvania 600-W projection lamp generates similar amounts of epoxide **2** and fluorenone **3**. Irradiation of **1** in the absence of oxygen, or attempted oxygenation of **1** in the absence of light, led, in the same length of time, to no observable products.

The photooxidation of **1** is unaffected by added sensitizer, tetraphenylporphin (TPP), whereas the photooxidation of 2,3-dimethyl-2-butene present in the same solution is greatly accelerated in the presence of TPP (Table I). These results indicate that free singlet oxygen plays no role in the photooxidation of **1**.

The oxidation of **1** is further characterized by the following observations: (a) as reaction temperature is lowered, epoxide yield diminishes (Table II); (b) the product ratio at 25 °C is almost independent of the initial concentration of **1** (Table III); (c) the quantum yield for the photooxidation in carbon tetrachloride at 3300 Å is about 12; (d) the photooxidation is unappreciable in benzene, but proceeds rapidly in benzene with small amounts of carbon tetrachloride added (Table IV).

The large effect of carbon tetrahalides in this reaction, not just as solvents but when present in dilute solution in benzene, recalls the position of these compounds as chain transfer agents in free-radical reactions. For example, in the polymerization of styrene at 60 °C carbon tetrachloride and carbon tetrabromide have chain transfer constants of 0.009 and 1.36, respectively.[6] A step where chain transfer might be of significance in the photooxidation of **1** would be the possible conversion of a biradical **4** into a halogenated monoradical **5** capable of giving chain character to the oxidation:



4 **5**

In order to test whether the radical **5** plays a role in this oxidation or not, the related bromohydroperoxide **5H** (X = Br) was prepared from **1** by the method of Kopecky.[11]

Table II. Ratio of Products from the Photooxidation of **1** in Carbon Tetrachloride as a Function of Temperature[a]

Temp, °C	Time, min	% reaction	Product composition % **2**	Product composition % **3**
−20	30	96	4	96
4	45	97	9	91
24	45	67	40	60
75	60	85	72	28

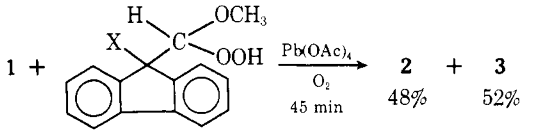
[a] **1** initially 0.48 M in all experiments; light source, Sylvania 600-W projection lamp.

Table III. Effect of Initial Concentration of **1** on the Photooxidation[a] Product Ratio

Initial **1**	% reaction in 15 min		% **2**		% **3**	
0.095	41		45		55	
0.048	66		53		47	
0.021	85	av 89	47	av 50	53	av 50
0.021	92		54		46	
0.021	91		49		51	
0.0095	Complete		55		45	

[a] Irradiations performed in a Rayonet miniphotochemical reactor ("merry-go-round") with a 3500-Å lamp at 25 °C.

Indeed the conversion of **1** to **2** and **3** can be initiated thermally by the oxidation of catalytic amounts of bromohydroperoxide **5H** (X = Br) with lead tetraacetate in the presence of **1** and oxygen, in the dark. Since lead tetraacetate is a general reagent for producing peroxy radicals from hydroperoxides,[7] this experiment supports the participation of the haloperoxy radical **5** in the photooxidation. In the thermally initiated reaction, one bromohydroperoxide molecule causes the conversion of 8–9 molecules of **1** to oxidation products. In the absence of **1**, the oxidation of **5H** with lead tetraacetate leads mainly to fluorenone.



5H
7.5%

(1)

Discussion

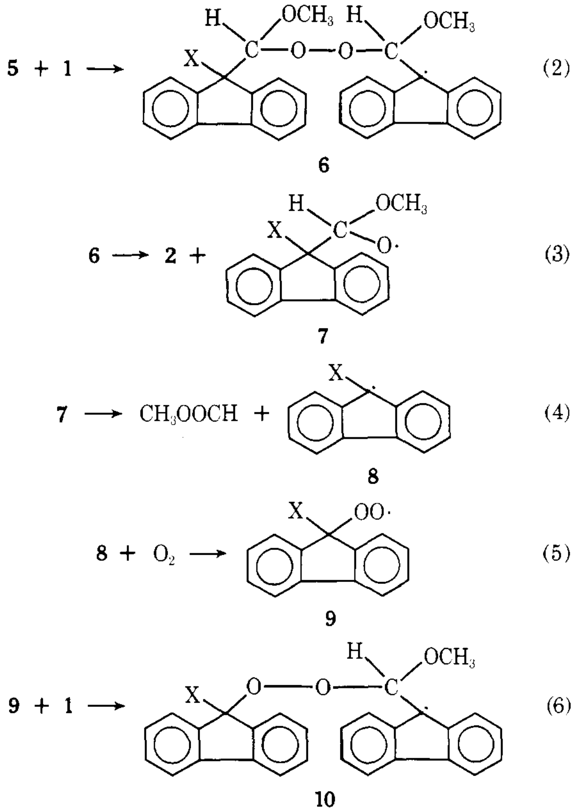
The results of Table I show that little, if any, singlet oxygen is generated during the unsensitized photooxidation of **1**. The essential role of carbon tetrahalides and the quantum yield of 12 both indicate that in this photooxidation a chain reaction is occurring. The combination of epoxide formation and oxidative cleavage recalls such classical cases as the free radical initiated autoxidation of styrene,[9] in which each interrupted polymerization chain leads to one epoxide molecule and a number of molecules of cleavage product. If the Mayo chain mechanism can be applied to the present case, it must be modified to take care of important differences in the reactions. Unlike styrene, methoxymethylenefluorene does not form a high polymer; neither end of the double bond presents the favorable free-radical attack site required for a long chain copolymerization mechanism. Experimentally the epoxide, which in the case of styrene is suppressed except at very low oxygen pressures, becomes the major product in the case of **1** at 1 atm of oxygen.

A reasonable explanation of these differences arises from the presence of a halogen atom on each radical participating in the oxidation process. If **1** enters only slowly into polymer chain growth, but the processes of chain cleavage and peroxy radical coupling proceed normally, then as a first approximation no radical will become larger than **6**, and the relative yields of products **2** and **3** will be determined by the relative rates of steps 2 and 8 (k_2/k_8) and of steps 6 and 9 (k_6/k_9),

Table IV. Effect of CCl_4 and CBr_4 in Photooxidation of **1** (0.021 M) at 25 °C

Solvent	Added	Conditions	% rxn	% **2**	% **3**
1. Benzene		Carousel[a] 15 min	None		
2. Benzene	0.4 M CCl_4	Carousel[a] 15 min	49	23	26
3. Benzene	0.1 M CCl_4	Carousel[a] 15 min	17	7	10
4. Benzene	0.09 M CBr_4	Carousel[a] 15 min	64	36	28
5. Benzene	0.00158 M **5H** 0.00168 M $Pb(OAc)_4$	Dark O_2	67	32	35

[a] Irradiated with a 3500-Å mercury arc, solutions continuously saturated with oxygen. Samples 1 and 2 were run simultaneously as were samples 3 and 4.



$$10 \longrightarrow 2 + 3 + X\cdot \qquad (7)$$

$$5 + 5 \longrightarrow O_2 + 7 + 7 \qquad (8)$$

$$9 + 9 \longrightarrow O_2 + 3 + 3 + 2X \qquad (9)$$

Termination by any pair: X·, **5**, **6**, **7**, **8**, **9**, **10** (10)

since these ratios determine whether **5** and **9**, respectively, will react with or without producing any epoxide.

For simplicity in the above equations, we have not shown the tetroxide intermediate[7,13] in steps 8 and 9, and we intend to include in the possibilities of step 10 any concerted Russell termination[14] proceeding directly from this tetroxide and leading to the disproportionation products of **7**.

To the extent to which reactions 8 and 9 take the indicated course they are not chain terminating (as they are when alkoxy radical pairs couple or disproportionate), but they lead to free halogen atoms which initiate new reaction chains. The alkoxy radicals related to **5** and **9** probably undergo β-fission more favorably than the corresponding radicals in the autoxidation of styrene. The regiochemistry of methoxymethylenefluorene is not critical to the formation of the indicated products; the halogen atom could attack the double bond at either end with the same eventual results.

There is thus a possible explanation of the relatively sharp effect of temperature on the product composition. At low temperatures peroxy radical coupling prevails, and the favored reactions 4, 5, and 9 give methyl formate and fluorenone only. At higher temperatures reaction 2 competes favorably and the sequence 3–7 leads to a 2:1 ratio of **2** and **3**. In addition, the CX_3 radical generated in the original reaction of CX_4 could form a peroxy radical and, with **1**, yield an epoxide molecule without an accompanying ketone.

This mechanism requires that reactions 7 and 9, which return chlorine atoms to the solution, must occur 8–12 times more frequently than all forms of reaction 10.

The product composition $P = (\mathbf{2})/(\mathbf{3})$ depends upon the fate of the radicals **5** and **9** in the following manner: if all of **5** couples, $P = 0$; if **5** adds **1** and **9** couples, $P = 1$; if **5** and **9** always add **1**, $P = 2$. The observed range of P at 25 °C, 0.8–1.2, and its insensitivity to concentration of **1** are intelligible if **1** is capturing a large fraction of **5** and only a small fraction of **9**.

The possibility must also be considered that the epoxide **2** and the dioxetane of **1** (as a precursor of cleavage products) might arise by S_Hi reactions of the radicals **7** and **5**, respectively, with intramolecular displacement of chlorine atom. Trahanovsky and Doyle[15] and Garst and Barbas[16] have examined some potentially favorable cases of intramolecular displacement of halogen by a carbon radical, and have concluded that this reaction does not occur.[17] In view of the rapid cleavage and coupling processes with which this reaction would have to compete in the present case, the estimated[18] endothermicities of 25 and 36 kcal/mol, respectively, make this appear a very unfavorable case for the occurrence of an S_Hi process.

Experimental Section

All ^1H NMR spectra were recorded on a Varian HA-60 or a JEOL MH-100 NMR spectrometer; all IR spectra were recorded on a Beckman IR-33 infrared spectrometer; mass spectra were obtained on a Finnigan 1015 S/L mass spectrometer; and all UV spectra were recorded on a Cary-15 spectrophotometer. 9-(Methoxymethylene)-fluorene was prepared from 9-fluorenecarboxaldehyde.[10] Carbon tetrachloride (Mallinckrodt) was used without additional purification. Carbon tetrabromide (Eastman) was purified by sublimation.

Preparation of the Oxirane of 9-(Methoxymethylene)fluorene (2). *m*-Chloroperbenzoic acid (Aldrich, 1.0 g of 85%, 5.0 mmol) was added to 0.461 g (2.0 mmol) of 9-(methoxymethylene)fluorene in 20 mL of ether. The solution was allowed to stand at room temperature for 10 min and was then washed with three 20-mL portions of 10% aqueous sodium sulfite and with three 20-mL portions of 10% aqueous sodium bicarbonate. The ether layer was dried over magnesium sulfate, and solvent was removed at reduced pressure. The residue, a yellow oil, consisted predominantly of epoxide **2**; a small amount of enol ether **1** and several unidentified products were also present in the crude product. Purification on alumina at −78 °C with dichloromethane as eluent gave 0.23 g (51%) of **2** as a pale yellow oil: NMR (CCl_4) δ 3.72 (s, 3 H), 5.10 (s, 1 H), and 7.2–7.8 (m, 8 H); IR (salt plate) 3100 (m), 3040 (w), 2980 (m), 2860 (w), 1620 (m), 1500 (w), 1460 (s), 1420 (m), 1340 (w), 1310 (w), 1221 (s), 1190 (s), 1100 (s), 1070 (m), 995 (m), 900 (m), 750 cm^{-1} (s); mass spectrum parent peak at *m/e* 224.

Preparation of the Bromohydroperoxide (5H) of 9-(Methoxymethylene)fluorene. Bromohydroperoxide **5H** was prepared in a manner similar to that reported by Kopecky et al.[11] for the preparation of 2-bromo-3-hydroperoxy-2,3-dimethylbutane. 9-(Methoxymethylene)fluorene (441 mg, 2.12 mmol) was dissolved in 25 mL of ether and cooled to −40 °C. Hydrogen peroxide (90%) (FMC, 4.5 g, 125 mmol) was added, followed by the addition of 318 mg (2.13 mmol of Br^+) of 1,3-dibromo-5,5-dimethyl-1,3-hydantoin (Baker Chemical Co.). The reaction mixture was kept at −40 °C for 25 min and was then allowed to warm slowly to room temperature. The solution was washed with 25 mL of 10% aqueous sodium bicarbonate. Solvent was removed at reduced pressure, affording a light yellow solid. The crude product was recrystallized at −78 °C in 15 mL of dichloromethane-pentane (1:2 v/v), yielding 403 mg (60%) of bromohydroperoxide **5H** as a pale yellow solid: NMR ($CDCl_3$) δ 3.58 (s, 3 H), 5.12 (s, 1 H), 7.1-7.7 (m, 8 H), and 8.4 (s, 1 H); IR (thin coating on a salt plate) 3340 (s), 3040 (w), 2950 (m), 2860 (w), 1600 (w), 1450 (m), 1400 (m), 1360 (m), 1310 (m), 1190 (m), 1080 (s), 1040 (s), 970 (w), 910 (w), 870 (m), 820 (m), and 720 cm^{-1} (s). Titration for peroxide content[12] of **5H** consistently yielded values of 100-105% of the theoretical value.

Photooxidations of 9-(Methoxymethylene)fluorene (1). A. Typical Procedure. A solution of 0.208 g (1.0 mmol) of **1** in 10 mL of carbon tetrachloride was continuously saturated with oxygen and irradiated at 25 °C with a Rayonet 3500-Å lamp in a Rayonet miniphotochemical reactor ("merry-go-round"). A second solution of 0.208 g of **1** in 10 mL of carbon tetrachloride was purged with nitrogen and irradiated simultaneously with the oxygenated solution. After 45 min, the oxidized solution showed the following product composition: 6% unreacted **1**, 52% fluorenone, and 42% epoxide **2**. Product analysis was determined by evaluating integrations of the methoxy absorptions of **2** (δ 3.72) and of **1** (δ 4.02) relative to that for total aromatic absorptions, with % fluorenone = 100% − % **1** − % **2**. The nitrogen-purged solution showed only small amounts of oxidation products (~3% of each product).

The oxidized solution was chromatographed on alumina at −78 °C with dichloromethane as eluent. **2** (71 mg, 32%) was isolated in this manner (elutes before an intensely yellow band, fluorenone) and was shown to be identical with an authentic sample (by comparison of NMR and IR spectra). Fluorenone (91 mg, 50%) was also isolated. For fluorenone: NMR (CCl_4) multiplet at δ 7.2-7.8, IR (0.1-mm cell vs. CCl_4) 3100 (m), 2950 (m), 1470 (s), 1620 (s), 1470 (m), 1310 (m), 1270 (w), 1200 (m), 1160 (w), 1100 (m), and 920 cm^{-1} (m).

B. In Benzene with and without Added Carbon Tetrachloride or Carbon Tetrabromide. Two solutions were prepared. Solution A consisted of 44 mg (0.21 mmol) of 9-(methoxymethylene)fluorene (**1**) in 10 mL of benzene; solution B consisted of 44 mg (0.21 mmol) of **1** in 10 mL of benzene and 400 μL (4 vol %) of carbon tetrachloride. The solutions were continuously saturated with oxygen and irradiated (simultaneously, with a 3500-Å lamp) in a "merry-go-round" apparatus for 15 min. Solvent was then removed from each solution and product analysis (NMR) was performed as previously described. Solution A (benzene) had not undergone reaction while solution B (benzene + 4% carbon tetrachloride) had undergone substantial photooxidation: 49% reaction, of which 53% was fluorenone and 47% was epoxide **2**.

In a separate experiment, two solutions were competitively photooxidized for 15 min (at 3500 Å) as before: solution A, 44 mg (0.21 mmol) of **1** in 10 mL of benzene with 100 μL (1 mmol) of carbon tetrachloride; solution B, 44 mg (0.21 mmol) of **1** in 10 mL of benzene with 300 mg (0.09 mmol) of freshly sublimed carbon tetrabromide. For solution A, 17% reaction, of which 58% was fluorenone and 42% was **2**; for solution B, 64% REACTION= OF WHICH 44% was fluorenone and 56% was **2**.

C. Effect of Initial Concentration of 1 on the Distribution of Oxidation Products. Four solutions were prepared: (1) 200 mg (0.95 mmol) of **1** in 10 mL of CCl_4 (0.095 M); (2) 100 mg (0.48 mmol) of **1** in 10 mL of CCl_4 (0.048 M); (3) 44 mg (0.21 mmol) of **1** in 10 mL of CCl_4 (0.021 M); (4) 20 mg (0.095 mmol) of **1** in 10 mL of CCl_4 (0.0095 M). In separate experiments, each solution was continuously saturated with oxygen and irradiated as before in a "merry-go-round" apparatus at 3500 Å. Reaction temperature was 25 °C and irradiation time was 15 min in all experiments. Oxidation of solution 3 was repeated (three experiments) to test for reproducibility. NMR analyses of reaction mixtures as previously described indicated the following product compositions: for 1, 55% fluorenone and 45% **2** at 41% completion; for 2, 47% fluorenone and 53% **2** at 66% completion; for 3, 53% fluorenone and 47% **2** at 85% completion (expt 1), 46% fluorenone and 54% **2** at 92% completion (expt 2), and 51% fluorenone and 49% **2** at 91% completion (expt 3); for 4, 45% fluorenone and 55% **2** at completion.

D. With and without Added Sensitizer Tetraphenylporphin (TPP). A solution of 200 mg (0.96 mmol) of **1**, 100 mg of bibenzyl (internal standard), and 80 mg (0.95 mmol) of 2,3-dimethyl-2-butene (**11**) in 5 mL of carbon tetrachloride was continuously saturated with oxygen and irradiated with a 600-W Sylvania projection lamp for 15 min. The NMR spectrum of the reaction mixture indicated the presence of 35% **2**, 20% fluorenone, 45% unreacted **1**, and 80% of initial **11** (20% loss due to volatilization). No detectable 2,3-dimethyl-3-hydroperoxy-1-butene (**12**), the sole product of the reaction of singlet oxygen[1c] with **11**, was observed.

A solution of 200 mg (0.96 mmol) of **1**, 100 mg of bibenzyl (internal standard), and 80 mg (0.95 mmol) of 2,3-dimethyl-2-butene (**11**) in 5 mL of carbon tetrachloride with 8.5×10^{-4} M TPP (as sensitizer) was continuously saturated with oxygen and irradiated with a Sylvania 600-W projection lamp for 5 min. The NMR spectrum of the irradiated solution indicated the following product composition: 70% unaltered **1**, 12% **2**, 18% fluorenone, 93% allylic hydroperoxide **12**, and 5% initial **11**.

Product analyses (for both experiments) were evaluated by integrations (before and after oxidation) of the methoxy groups of **1** (δ 4.02) and **2** (δ 3.72) and of the methyl groups of **11** (δ 1.60) and **12** (two equivalent methyls at δ 1.28) relative to that of the internal standard, bibenzyl (two equivalent methylenes at δ 2.83). The yield of fluorenone was determined by % fluorenone = 100% − % **1** − % **2**.

E. Effect of Temperature on the Ratio of Oxidation Products. Four solutions, each containing 100 mg (0.48 mmol) of **1** in 1 mL of carbon tetrachloride in a 5-mL round-bottom flask, were continuously saturated with oxygen and irradiated with a Sylvania projection lamp (600 W). Each solution was irradiated at a different temperature: 1 at −20 °C (dry ice cooled acetone bath); 2 at 4 °C (ice-water); 3 at 24 °C (water bath); and 4 at 75 °C (hot water bath). NMR analyses of the reaction mixtures indicated the following product compositions: after 30 min, solution 1 was oxidized to 96% completion with fluorenone and methyl formate (doublet at δ 3.66, 3 H, J = 0.4 Hz, and quartet at δ 7.90, 1 H, J = 0.4 Hz) as the major products (96% vs. 4% of **2**); after 45 min, solution 2 was oxidized to 97% completion, of which 9% was **2** and 91% was fluorenone; after 45 min, solution 3 was oxidized to 67% completion, of which 40% was **2** and 60% was fluorenone; and after 60 min, solution 4 was oxidized to 85% completion, of which 72% was **2** and 28% fluorenone.

Determination of the Quantum Efficiency of the Photooxidation of 1 in Carbon Tetrachloride at 3300 Å. A. Determination of Light Intensity at 3300 Å. The intensity of light at 3300 Å from a Bausch and Lomb SP-200 mercury light source with a Bausch and Lomb grating monochromator was determined with ferrioxalate actinometry.[8] Solutions of potassium ferrioxalate (0.006 M) were placed in two 1-cm (3 mL capacity) quartz cuvettes. The two cuvettes were taped together (total optical length, 2 cm), placed directly in front of the light-beam exit of the monochromator, and irradiated for 500 s. Yields of ferrous ions were determined by spectrometric analysis of the red ferrous ion phenanthroline complex (λ_{max} at 5100 Å). More than 95% of the photoreduction occurred in the front cell (closer to light-beam exit), with little (<5%) photoreduction occurring in the back cell. The intensity of the light at 330 nm was then determined as 1.14×10^{15} quanta/s.

B. Determination of the Quantum Yield. 1 (54 mg) was dissolved in 3 mL of carbon tetrachloride and placed in a 1-cm quartz cuvette. The ferrioxalate solution (3 mL, 0.05 M) was placed in a second 1-cm quartz cuvette. The two cuvettes were taped together and placed in front of the light-beam exit of the monochromator, with the solution of olefin directly in front of the exit. The solution of **1** was continuously saturated with oxygen and irradiated at 3300 Å for 1500 s. Solvent was removed from the oxidized solution at reduced pressure and the percentage of reaction determined by NMR analysis as previously described: 13% reaction, 7% epoxide **2**, and 6% fluorenone (87% starting olefin). Analysis of the back cuvette (of the ferrioxalate solution) indicated the absence of ferrous ions, indicating complete absorption of the incident light in the front cell. The quantum yield of photooxidation ($\phi_{ox}{}^{3300}$) at 3300 Å was then determined as follows:

$$\phi_{\text{ox}}{}^{3300} = \frac{\text{no. of molecules reacted}}{\text{no. of photons absorbed}}$$

$$\text{No. of molecules reacted} = \frac{\text{wt}}{\text{mol wt}} \times A \times \text{yield}$$

$$= \frac{0.054}{208} \times 6.023 \times 10^{23} \times 0.13$$

$$= 2.03 \times 10^{19}$$

$$\text{No. of photons absorbed in 1500 s} = 1.14 \times 10^{15} \times 1.5 \times 10^{3}$$

$$= 1.71 \times 10^{18}$$

$$\phi_{\text{ox}}{}^{3300} = \frac{2.03 \times 10^{19}}{1.71 \times 10^{18}} = 11.9$$

Reaction of Bromohydroperoxide 5H (X = Br). A. With Lead Tetraacetate. Lead tetraacetate (66 mg, 0.15 mmol) (Matheson Coleman and Bell) was added to 32 mg (0.1 mmol) of bromohydroperoxide **5H** in 10 mL of benzene with 100 mg of sodium carbonate. The solution was stirred at room temperature for 5 min, purged with 10 mL of ether, and washed with three separate 10-mL portions of water. The organic layer was dried over magnesium sulfate, and solvent was removed at reduced pressure. The NMR spectrum of the residue indicated fluorenone as the major product. A small amount of a second, unidentified product was also observed. The crude product was purified on alumina with pentane-dichloromethane (4:1 v/v) as eluent. Fluorenone (9 mg, 50%) was isolated in this manner and was shown to be identical with an authentic sample (by comparison of NMR and IR spectra).

B. With Lead Tetraacetate in the Presence of 1. A solution of 208 mg (1.0 mmol) of **1**, 24 mg (0.075 mmol) of bromohydroperoxide **5H**, and 100 mg of sodium carbonate in 20 mL of benzene was continuously saturated with oxygen at room temperature. Lead tetraacetate (35 mg, 0.08 mmol) was added, and the resulting solution was stirred for 30 min. The reaction mixture was then purged with 20 mL of ether, washed with three separate 20-mL portions of water, and dried over magnesium sulfate. Solvent was removed at reduced pressure, and an NMR spectrum (CCl_4) of the residue (200 mg of a yellow oil) indicated the following product composition: 33% unreacted **1**, 32% **2**, and 35% fluorenone. Products were separated by low temperature (−78 °C) chromatography on alumina with dichloromethane as eluent as previously described and were shown to be identical with authentic samples (by comparison of NMR and IR spectra).

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Gas-Phase Aromatic Substitution by Positive Bromine Ions from ^{80m}Br(IT)^{80}Br: A Study of Linear Free Energy Relationship

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Abstract: Mono- and disubstituted benzenes have been brominated by $^{80}Br^+$ in the gas phase following the isomeric transition ^{80m}Br(IT)^{80}Br. The ratios of rates, derived from product ratios, give linear $\sigma\rho$ plots using σ^+ parameters with $\rho^+ = -0.9$. Inductive and resonance effects were separated to obtain $\rho_I{}^m = -0.78$, $\rho_I{}^p = -0.80$, $\rho_R{}^m = -0.20$ and $\rho_R{}^p = -1.03$. An extension of these results led to a quantitative analysis of additive influences of the substituents in the *p*-dichlorobenzene molecule. Following the empirical formula $\log p_f{}^{Me} = c \log (p_f{}^{Me}/m_f{}^{Me})$ in the toluene system, a correlation between the experimental results and the theory is given by the expression $c = \sigma_p{}^+/(\sigma_p{}^+ - \sigma_m{}^+)$. The fact that our results of the electrophilic substitution by $^{80}Br^+$ follow the "classical" reactivity–selectivity relationship seems to be a good proof for the validity of a linear free energy relationship even for extremely reactive electrophilic species like unsolvated ions in the gas phase. Obviously the naked ions follow a similar mechanism as solvated ions and there is no need for establishing a new reaction model for the gas-phase aromatic substitution.

A number of kinetic and mechanistic studies of ionic gas-phase reactions in aliphatic and aromatic systems has been performed in the last years by various laboratories.[1-6] All kinetic results were obtained by mass spectrometric techniques, including ICR or by radiolytic methods. Little information, however, is known about kinetic studies using methods of