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Catalytic Behavior of Sulfonium Trihalides in the Low-temperature Liquid-phase Oxidation of Tetralin

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Synopsis. Homogeneous oxidation of nonpolar tetralin catalyzed by sulfonium trihalides was found to proceed *via* a radical chain mechanism in which the trihalide catalysts promoted the reaction through the activation of molecular oxygen.

Although numerous investigations have hitherto been performed on the bond property of trihalide ions with the conclusion that the trihalide ions can be well explained by their Rundle 3c-4e (three center four-electron) bonds without the participation of d-orbitals to their almost covalent linear bonds,[1] onium trihalides, especially of the sulfonium type, have received only limited attention in terms of their chemical reactivity in solutions. An interesting chemical property of sulfonium trihalides has recently been found in this laboratory: their remarkable catalytic activity in the low-temperature liquid-phase oxidation of hydrocarbons. In this paper, experimental and MO-theoretical studies of the sulfonium trihalides are reported with a view of examining how they accelerate the liquid-phase oxidation of hydrocarbons.

Experimental

Materials and Experimental Procedure. The triphenylsulfonium and tetrabutylammonium compounds used as oxidation catalysts were prepared by the usual methods.[2-4] A portion (10 ml) of the fresh distillate of tetralin was subjected to homogeneous liquid-phase oxidation with a catalyst (0.005 mmol) in the temperature range of 45—85 °C under atmospheric pressure. UV spectroscopic measurements of triphenylsulfonium trihalides were carried out in CH_3OH at 25 °C using Shimadzu 200 and Hitachi 200-10 spectrophotometers.[5]

Results and Discussion

Let us first examine the activities of several triphenylsulfonium trihalides for homogeneous oxidation of tetralin at 65 °C. As can be seen from Table 1, the sulfonium trihalides markedly accelerate the oxidation rate with no induction period (in an autocatalytic fashion) resulting in a monotonic accumulation of tetralin hydroperoxide (HPO) only as an oxidation product, although tetralin autoxidation indicated an induction period of 24 min. Also, the sulfonium trihalides are more active than ammonium salts having the corresponding trihalide anions. It is also noteworthy that the maximum O_2-absorption rate ($R_{\max}$) appearing during the initial short reaction stage (up to 7 min) without appreciable decomposition of HPO showed a first-order dependence on the concentration of the sulfonium trihalide and that more than 85% of the trihalide can be recovered from the reaction mixture after a reaction time of about 15 min.[6] From these observations the following dissociation of sulfonium trihalide ($R_3SX^1X^2X^3$: X^2=middle halogen and X^1=X^3=terminal halogen) into sulfonium monohalide (R_3SX^2) and a halogen molecule (X^1X^3), within a reaction time of up to 10 min, is not believed to be very important:

$$R_3SX^1X^2X^3 \overset{K}{\rightleftharpoons} R_3SX^2 + X^1X^3 \tag{1}$$

where K is an equilibrium constant, and X^2 is assumed to be more electronegative than either X^1 or X^3. The dissociation of $R_3SX^1X^2X^3$ is also not expected in such nonpolar hydrocarbons as tetralin, in view of the fact that the K values are very small even in $CHCl_3$ at 20 °C (about 10^{-5}—10^{-4} mol/l[4]).

Now, we consider how $R_3SX^1X^2X^3$ initiates the present oxidation reaction which was confirmed to proceed *via* the usual radical-chain mechanism. The formation of radical initiators through the decomposition of peroxides (ROOH) by $R_3SX^1X^2X^3$ does not occur during the initial short reaction stage, because ROOH is monotonically accumulated in amount (mol) corresponding almost quantitatively to the oxygen absorbed (mol) and because the addition of ROOH to the reaction system markedly depressed the reaction rate. These results are due to the promotion of the dissociation of $R_3SX^1X^2X^3$ or partly due to the blocking effect by species containing lone-pair electrons against interaction of the oxidation catalyst ($R_3SX^1X^2X^3$ or R_3SX^2) with O_2 (see later).[7] The dissociation products (R_3SX^2 and X^1X^3) in equimolar amounts did not initiate the reaction in spite of the existence of effective oxidation catalysts (R_3SX^2) in the reaction system. This might also be due to the above-mentioned blocking effect of X^1X^3.

The markedly higher activity of $R_3SX^1X^2X^3$ as compared with the ammonium trihalides, despite the nearly identical K values (*ca.* 10^{-4} mol/l[4]) in $CHCl_3$ at 20 °C) of ammonium trihalide as that of $R_3SX^1X^2X^3$ does not support the halide-anion catalysis which is expected in ammonium halides.[8]

The following initial step, in which $R_3SX^1X^2X^3$ accelerates the reaction *via* the activation of O_2, appears to be most reasonable in connection with the catalytic behavior of R_3SX for hydrocarbon oxidation:[5,8,9]

$$R_3SX^1X^2X^3 + O_2 \rightleftharpoons [R_3S(X^1X^2X^3)^{\delta+}\cdots O_2{}^{\delta-}] \xrightarrow{RH} R\cdot + HO_2\cdot + R_3SX^1X^2X^3 \tag{2}$$

If Reaction 2 is plausible, one can expect direct interaction between $R_3SX^1X^2X^3$ and O_2, and hence, some specific orbitals of the former should play an important role in the activation of the latter. In regard to the interaction molecular oxygen appreciably shifts the

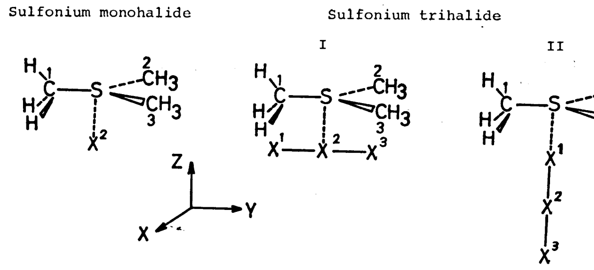

Fig. 1. Molecular structures of $(CH_3)_3SX^1X^2X^3$ and $(CH_3)_3SX^2$ (S-C(fixed bond-length in the calculation) = 1.82 Å; ∠CSC = 120°; S-X^2 or S-X^1 = purely ionic distance; X^1-X^2 or X^2-X^3 = purely covalent distance.)

sulfur $(3p)^2 \rightarrow (3p)(3d)$ transition (λ_{max} = 208—210 nm and $\log \varepsilon$ = 4.61—4.72 in CH_3OH at 25 °C in an N_2 atmosphere) of the sulfonium cation[10] to longer wavelengths over an energy scale from 0.03 to 0.09 eV. This implies that the lowering of the partially-occupied sulfur d-orbitals (see below), which results from charge transfer from the d-orbitals (especially, the d_{xz} orbital in Fig. 1) to O_2, simplifies the above-mentioned electron excitation mechanism. In this sense, it can be believed that the more the electron density of the d_{xz} orbital increases, the higher becomes the catalytic activity (as reflected in the R_{max} value) of $R_3SX^1X^2X^3$. In fact, as Fig. 2 indicates, the R_{max} values of $R_3SX^1X^2X^3$ (and R_3SX) show a correlation with the electron densities of the d_{xz} orbital which is favorably distributed for interaction with the $(1\pi_g)_z$ orbital of O_2.[9]

Table 1. Catalytic activitities of triphenylsulfonium trihalides (0.005 mmol) in tetralin (10 ml) oxidation at 65 °C

Compound	(O_2)absd[a] (mmol)	HPO[b] (%)	10^4R_{max} (M/s)	Compound	(O_2)absd[a] (mmol)	HPO[b] (%)	10^4R_{max} (M/s)
$(C_6H_5)_3SBrClBr$	0.95	99.4	0.61	$(C_6H_5)_3SClICl$	0.70	99.7	0.42
$(C_6H_5)_3SIClI$	0.93[c]	99.8[a]	0.75[c]	$(C_6H_5)_3SBrIBr$	0.66	99.4	0.35
	0.59	99.5	0.49	$(C_6H_5)_3SI_3$	0.60	99.7	0.35
	0.41[d]	99.7[d]	0.25[d]	$(C_6H_5)_3SI$	0.78	99.0	0.61
	0.26[e]	99.5[e]	0.20[e]	$(C_6H_5)_3SBF_4$	0.18	100	0.17
$(C_6H_5)_3SCl$	1.08	99.2	1.19	$(n\text{-}C_4H_9)_4NBrClBr$	0.26	100	0.17
$(C_6H_5)_3SClBrCl$	0.82	99.8	0.53	$(n\text{-}C_4H_9)_4NBr_3$	0.21	100	0.15
$(C_6H_5)_3SBr_3$	0.76	99.4	0.50	$(n\text{-}C_4H_9)_4NBF_4$	0.05	100	0.05
$(C_6H_5)_3SIBrI$	0.91	99.2	0.52	none	0.01[f]	100[f]	0.01[f]
$(C_6H_5)_3SBr$	0.94	99.5	0.83				

a) After a reaction time of 30 min. b) Based on the O_2 absd (mmol). c) At 85 °C. d) At 55 °C. e) At 45 °C. f) The incubation period was 24 min.

Table 2. UV transition energies and formal charges of $X^1X^2X^3$ ions in $R_3SX^1X^2X^3$

Compound	Transition energy of $X^1X^2X^3$	Formal charge			
		X^2		$X^1 = X^3$	
	Obsd[a] (Calcd) (eV)	Obsd	(Calcd)	Obsd	(Calcd)
$(C_6H_5)_3SBrClBr$	4.63 (4.78)	—	(0.29)	—	(−0.39)
$(C_6H_5)_3SIClI$	4.28 (4.23)	—	(0.22)	—	(−0.45)
$(C_6H_5)_3SClBrCl$	4.88 (5.20)	—	(0.35)	−0.56[b]	(−0.46)
$(C_6H_5)_3SBr_3$	4.64 (4.99)	0.06[c]	(0.30)	−0.34[c]	(−0.41)
$(C_6H_5)_3SIBrI$	4.25 (4.53)	—	(0.24)	—	(−0.46)
$(C_6H_5)_3SClICl$	5.35 (4.49)	0.29[d]	(0.31)	−0.62[d]	(−0.51)
$(C_6H_5)_3SBrIBr$	4.64 (4.39)	0.19[e]	(0.25)	−0.50[e]	(−0.47)
$(C_6H_5)_3SI_3$	4.28 (3.86)	0.05[e]	(0.20)	−0.51[e]	(−0.49)

a) From $(C_6H_5)_3SX^1X^2X^3$ in CH_3OH at 25 °C. b) E. F. Riedel and R. D. Willett, *J. Am. Chem. Soc.*, **97**, 701 (1975). c) G. L. Breneman and R. D. Willett, *J. Pyhs. Chem.*, **71**, 3084 (1967). d) S. Hagiwara, K. Kato, Y. Abe, and M. Minematsu, *J. Phys. Soc. Jpn.*, **12**, 1166 (1957); J. C. Evans and Y. G. S. Lo, *Inorg. Chem.*, **6**, 836 (1967). e) G. A. Bowmaker and S. Hacobian, *Aust. J. Chem.*, **21**, 551 (1968).
The calculated values were obtained from $(CH_3)_3SX^1X^2X^3$.

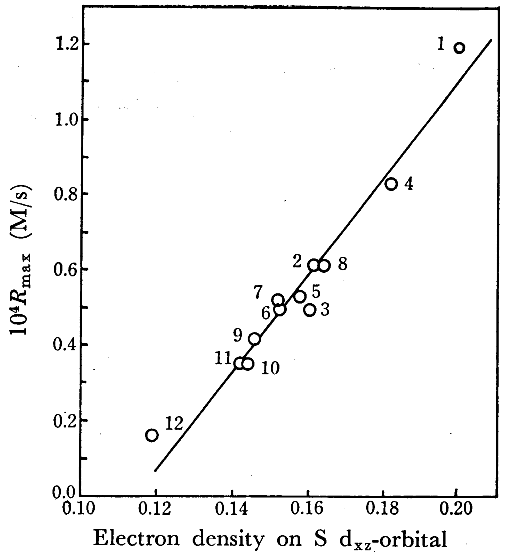

Fig. 2. Correlation between R_{max} values and electron densities on S d_{xz}-orbital.
1: $(C_6H_5)_3SCl$, 2: $(C_6H_5)_3SBrClBr$, 3: $(C_6H_5)_3SIClI$,
4: $(C_6H_5)_3SBr$, 5: $(C_6H_5)_3SClBrCl$, 6: $(C_6H_5)_3SBr_3$,
7: $(C_6H_5)_3SIBrI$, 8: $(C_6H_5)_3SI$, 9: $(C_6H_5)_3SClICl$,
10: $(C_6H_5)_3SBrIBr$, 11: $(C_6H_5)_3SI_3$, 12: $(C_6H_5)_3SBF_4$.

Finally, it is worthy of notice that the ASMO-SCF calculations[11] of $R_3SX^1X^2X^3$, as $(CH_3)_3SX^1X^2X^3$ for computation simplicity, resulted in reasonable electronic properties for energetically more stable $R_3SX^1X^2X^3$ (I in Fig. 1) in terms of the approximate coincidence between the calculation results and the spectroscopic (UV and NQR) observations (see Table 2).

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