Notes

Studies of Sulfonyl Radicals. 5.[1] Activation Energies for the Decomposition of Alkanesulfonyl Radicals

HO HUU THOI, MASASHI IINO, and
MINORU MATSUDA*

Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira 2-chome, Sendai, 980 Japan.

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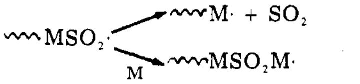
One of the peculiar features of the copolymerization of SO_2 and vinyl monomers is that the growing sulfonyl radical may undergo depropagation (process 1) as well as propagation (process 2)[2-7]



$$\sim\!\!\sim MSO_2\cdot \rightarrow \sim\!\!\sim M\cdot + SO_2 \quad (1)$$

$$\sim\!\!\sim MSO_2\cdot \xrightarrow{M} \sim\!\!\sim MSO_2M\cdot \quad (2)$$

where M stands for vinyl monomer. The relative rate of the two processes will therefore affect the composition of the resulting copolymer. An understanding of the mechanism of the copolymerization might be assisted by kinetic data on the two processes. In this study, we have taken the reaction of α-chloroethanesulfonyl chloride with styrene in the presence of $CuCl_2$ catalyst as a model reaction. This sulfonyl chloride is related to the copolymerization of SO_2 and vinyl chloride,[5-7] in which the structural formula of the growing sulfonyl radical is $\sim\!\!\sim CH_2CH(Cl)SO_2\cdot$. The mechanism of the reaction of sulfonyl chloride and styrene has been studied intensively by Orochov et al.,[8] who have proposed the following scheme:

$$CuCl + RSO_2Cl \rightleftarrows CuCl_2 + RSO_2\cdot \quad (3)$$

$$RSO_2\cdot \xrightleftharpoons{k_{dMS}} R\cdot + SO_2 \quad (4)$$

$$RSO_2\cdot + PhCH{=}CH_2 \xrightleftharpoons{k_{SM}} \underset{\text{I}}{RSO_2CH_2CH(Ph)\cdot} \quad (5)$$

$$R\cdot + CuCl_2 \rightarrow RCl + CuCl \quad (6)$$

$$\text{I} + CuCl_2 \rightarrow \underset{\text{II}}{RSO_2CH_2CH(Cl)Ph} + CuCl \quad (7)$$

In our study, R stands for CH_3– or $CH_3CH_2(Cl)$–. Assuming that the reverse of reactions 4 and 5 can be neglected enables us to derive relation 8 from eq 4 to 7,

$$[SO_2]/[\text{sulfone}] = k_{dMS}/k_{SM}[St] \quad (8)$$

where $[SO_2]$ and [sulfone] are the concentrations of SO_2 and sulfone II formed in the reaction, k_{dMS} and k_{SM} are the rate constants for the decomposition and addition, respectively, and [St] is the concentration of styrene, nearly equal to its initial concentration since the reaction was stopped at low conversion. Because the reaction was stopped at <20% conversion the concentration of SO_2 formed in the reaction is small enough that the addition of R· to SO_2 was neglected. Reaction 7 is so fast that the reverse of reaction 5 is also neglected. Experimentally, plots of the ratios of $[SO_2]$/[sulfone] vs. $[St]_0^{-1}$ in Figure 1 are straight lines, as expected from eq 8.

The slopes of the plots in Figure 1 yield the ratios of rate constants for the decomposition of α-chloroethanesulfonyl radical to its addition to styrene. These ratios of k_{dMS}/k_{SM} increase with increasing temperature. The results account for the results obtained in the copolymerization of SO_2 and vinyl chloride in which the SO_2 content of the copolymer falls off with the rise in temperature.[5-7] The Arrhenius plot in Figure 2 yields the difference in activation energies between the decomposition and the addition to be 11 ± 1.5 kcal/mol for the α-chloroethanesulfonyl chloride–styrene system.

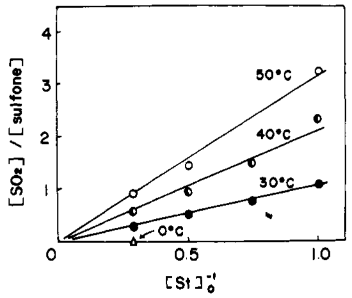


Figure 1. Plots of $[SO_2]$/[sulfone] vs. the inverse of initial styrene concentration at various temperatures for the reactions of α-chloroethanesulfonyl chloride with styrene.

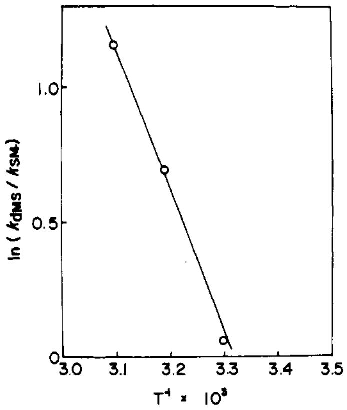


Figure 2. Arrhenius plot for the reactions of α-chloroethanesulfonyl chloride with styrene.

By a similar method, we have found that the difference in activation energies between the decomposition of the methanesulfonyl radical and its addition to styrene is 20 ± 2 kcal/mol but the plots are not shown here.

Good and Thynne[9] have reported that the value of the activation energy for the decomposition of the methanesulfonyl radical into methyl radical and SO_2 in the gas phase is 22.4 kcal/mol. If this gas-phase value also applies in solution, the activation energy for addition of methanesulfonyl radical to styrene is 2.4 kcal/mol. We further assume that the activation energy for addition of α-chloroethanesulfonyl radical to styrene is equal to that of methanesulfonyl radical, i.e., 2.4 kcal/mol; then the value of the activation energy for the decomposition of the former is calculated to be 13.4 kcal/mol. This assumption is reasonable because ESR[10] and electronic absorption spectroscopy[11,12] of sulfonyl radicals have shown that the unpaired electron of the sulfonyl radical is located mainly on the SO_2 moiety, so that the alkane or aryl moiety of sulfonyl radical should have little effect on the rate for the addition to double bonds. Takahara et al.[13] have shown that the rates of additions of sulfonyl radicals to vinyl monomers are independent of the structure of sulfonyl radical.

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Table I
Activation Energies for the Decomposition of Some Sulfonyl Radicals

sulfonyl radical	activation energy, kcal/mol	ΔE,[a] kcal/mol
$CH_3SO_2\cdot$[9]	22.4 ± 1.8	20.0 ± 2
$CH_3CH_2SO_2\cdot$[14]	19.9	
$CH_3CH(Cl)SO_2\cdot$[b]	13.4 ± 2.0	11.0 ± 1.5
$PhCH_2SO_2\cdot$[15]	12.0 ± 3.2	
$CH_2{=}CHCH_2SO_2\cdot$[15]	8.4 ± 3.2	

[a] The difference in activation energies between the decomposition and addition of sulfonyl radicals to styrene measured in this work. [b] Our estimated activation energy for decomposition.

For comparison purposes, data on the decomposition of some sulfonyl radicals reported by other workers are listed in Table I together with our results on the α-chloroethanesulfonyl radical. The decomposition of benzyl- and allylsulfonyl radicals is associated with low activation energy since the radicals formed in the decomposition are resonance stabilized. It is interesting to note that the activation energy for the decomposition of ethanesulfonyl radical is 6.5 ± 2 kcal/mol higher than that of α-chloroethanesulfonyl radical, which we attribute to the electrostatic repulsion between chlorine atom and SO_2 group.

Experimental Section

A solution of the catalyst (acetonitrile, 5 mL; $CuCl_2$, 0.175 g; $N(Et)_3HCl$, 0.250 g; AIBN, 0.150 g) was prepared.[8] A required amount of the catalyst solution (10 vol % of the total volume of reaction mixture) was then added to the reaction vessel containing benzene, styrene, and sulfonyl chloride. The molar ratio of styrene to sulfonyl chloride was 2. Benzene as diluent was used to vary the initial styrene concentrations, which were 1.0, 1.3, 2.0, and 3.5 M. The sample was thoroughly mixed and degassed. Reaction was homogeneous and was stopped at the desired times by cooling in a precooled methanol bath. A small amount of the reaction mixture was removed for determination of sulfone II by gas chromatography (GE-SE-30, 20% silicone oil on Chromosorb, 60–80 mesh, stainless steel column (2 m × 4 mm o.d.), column oven temperature 250 °C, injector temperature 300 °C). All the remainder was used for determination of SO_2 by iodide–thiosulfate titration.[16]

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References and Notes

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Equation of State for Crystalline Polyethylene

S. C. GEOL and V. S. NANDA*

Department of Physics and Astrophysics, University of Delhi, Delhi-110007, India

R. K. JAIN[1]

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.

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In a recent paper[2] a quantum mechanical version of the cell theory for polymeric solids, including the effect of anharmonicity in the cell potential to a first approximation, was given. The resulting equation of state was shown to describe quite nicely the variation of volume with temperature at atmospheric pressure for the crystal phase of polyethylene and poly(chlorotrifluoroethylene) over a wide range. It was also found that the isotherms of the semicrystalline polymer, on the basis of some plausible assumptions, were in accord with theory for temperatures sufficiently below the normal melting point. The direct data for the isotherm of the polyethylene crystal at room temperature of Ito[3] and Sham et al.[4] (SNP) have now become available to us. In the present note we examine the validity of our theory vis-â-vis their experimental results and the information about the P–V–T surface which was previously available. In doing so we have taken a fresh look at the values to be assigned to various parameters from the point of view of consistency regarding the values of the ratio c/n (the number of volume dependent degrees of freedom per repeat unit) derived from either (i) the assignment made for the scale factors for pressure (P^*), for volume (V^*), and for temperature (T^*) or (ii) the assignments for the reduced characteristic temperature $\tilde{\theta}_0$, T^*, and V^*.

In our earlier work[2] it was shown that the equation of state has the form

$$\tilde{P} = \tilde{P}(\tilde{V},\tilde{T},\tilde{\theta}_0,s/c) \qquad (1)$$

where $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are the reduced pressure, volume, and temperature respectively, while s and c are respectively the number of force centers and the number of volume dependent degrees of freedom per chain. For full details about the equation of state reference should be made to the previous paper.[2] In comparing theory with experiment, the values of parameters adopted there for polyethylene crystal, for $s/c = 1$, were $T^* = 6918$ K, $V^* = 0.9954$ cm^3 g^{-1}, $P^* = 18$ kbar, and $\tilde{\theta}_0(\tilde{V}_0) = 0.054$, $\tilde{V}_0$ being the reduced volume for $P = 0$ and $T = 0$ K. Using eq 2a and 4 of ref 2, it can be shown that

$$c/n = \frac{M_r}{N_A}\left\{\frac{1.5874\pi^2 k}{h^2}\right\}\frac{(T^*)^{3/5}(V^*)^{2/5}\tilde{\theta}_0{}^{6/5}\tilde{V}_0{}^{8/5}}{(A_1\tilde{V}_0{}^{-2} - 2B_1)^{3/5}} \qquad (2a)$$

where M_r is the molecular weight of the monomer repeat unit and N_A is the Avogadro's number. On the other hand, from the expressions for the scaling factors P^*, V^*, and T^* one gets

$$c/n = \frac{P^*V^*}{T^*}(M_r/R) \qquad (2b)$$

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