

Casanova. We are also grateful to Dr. Sukh Dev for a generous supply of *d*-longifolene.

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### THE ABSOLUTE RATE CONSTANT OF PROPAGATION OF ANIONIC POLYMERIZATION OF STYRENE<sup>1</sup>

Sir:

Anionic polymerization of styrene and of some other monomers, if carried out in a suitable solvent such as tetrahydrofuran, leads to formation of "living" polymers, *i.e.*, polymeric species which are not terminated and which retain their ability to grow.<sup>2,3</sup> The lack of termination in anionic polymerization enables one to determine the absolute value of the respective rate constant of propagation by applying the technique to be described. A solution of low molecular weight "living" polystyrene (mol. wt. 1000-2000) and a solution of monomeric styrene, both prepared in tetrahydrofuran, are introduced through capillaries into a T-shaped 3-way stopcock. A rapid mixing takes place in the barrel of the stopcock, and thereafter the reacting mixture flows through a third capillary into a beaker holding a solution of water or of methyl iodide dissolved in tetrahydrofuran. The polymerization which ensues on mixing the respective reagents is terminated instantly by their contact with the solution contained in the beaker, and the time of polymerization, determined by the capillary volume and the rate of flow, may be made as short as 0.1 sec.

TABLE I

RATE CONSTANT OF PROPAGATION OF "LIVING" POLYSTYRENE IN TETRAHYDROFURAN AT 25°; Na<sup>+</sup> IS COUNTER ION

Run	Initial concn. of "living" polymers in the capillary, moles/l.	Initial concn. of styrene in the capillary, moles/l.	<i>t</i> , sec.	% conversion	Rate constants moles <sup>-1</sup> sec. <sup>-1</sup>
1-1	0.486 × 10 <sup>-2</sup>	0.223	0.792	87.3	523
1-2	.486 × 10 <sup>-2</sup>	.222	.455	65.8	
1-3	.485 × 10 <sup>-2</sup>	.224	.305	53.9	
2-1	.340 × 10 <sup>-2</sup>	.097	.743	78.4	554
2-2	.337 × 10 <sup>-2</sup>	.098	.574	69.4	
2-3	.339 × 10 <sup>-2</sup>	.097	.447	56.9	
2-4	.337 × 10 <sup>-2</sup>	.098	.331	45.9	
3-1	.374 × 10 <sup>-2</sup>	.131	.750	78.2	545
3-2	.370 × 10 <sup>-2</sup>	.128	.551	67.6	
3-3	.370 × 10 <sup>-2</sup>	.127	.414	53.5	
3-4	.367 × 10 <sup>-2</sup>	.128	.310	45.2	
4-1	.379 × 10 <sup>-2</sup>	.130	.706	81.7	570
4-2	.373 × 10 <sup>-2</sup>	.132	.561	69.0	
4-3	.371 × 10 <sup>-2</sup>	.133	.400	57.9	
4-4	.368 × 10 <sup>-2</sup>	.134	.297	47.4	

(1) This work was supported by a grant from the National Science Foundation, G-14393, and by the Quartermaster Corp., Grant No. DA-19-129-QM-1297.

(2) M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

(3) M. Szwarc, *Nature*, **178**, 1168 (1956).

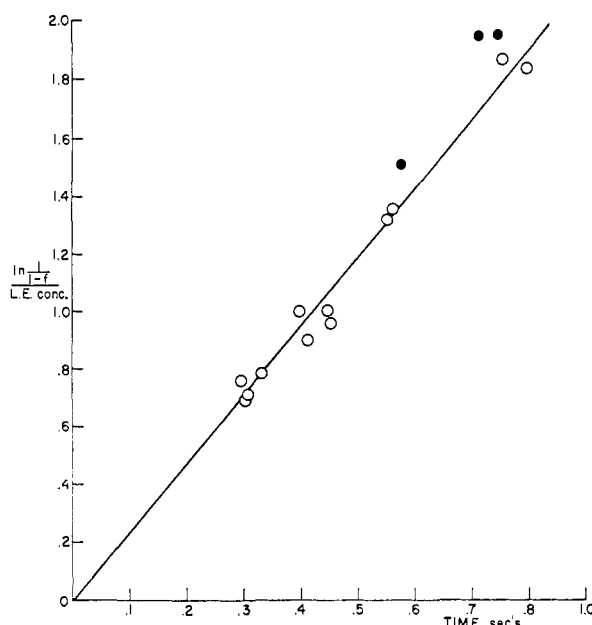


Fig. 1.—The black points were not taken into account in calculating the "least" square line.

The concentrations of the "living" ends and of the monomer are determined carefully at the beginning and at the end of each series of experiments. The rate of flow of each solution is measured directly and maintained constant in each run. Changing the pressure of pure nitrogen above each liquid permits one to vary the time of polymerization of an individual experiment. Both solutions are thermostated and the heat capacity of the reacting mixture is chosen in such a way that

TABLE II

DEPENDENCE OF  $k_p$  ON THE CONCENTRATION OF "LIVING" ENDS

System polystyrene in THF solution, counter-ion Na<sup>+</sup>, T is 25°

Concn. in moles/l. × 10 <sup>2</sup>	$k_p$ l. moles <sup>-1</sup> sec. <sup>-1</sup>
0.145	575
0.170	560
0.34	554
0.37	545
0.37	570
0.49	523
0.76	425
1.00	290
1.15	285

the adiabatic polymerization does not raise the temperature by more than 1°. The conversion of the monomer into polymer is determined directly, and the results obtained in four series of experiments are given in Table I and in Fig. 1. Since the concentration of "living" ends remains constant in each experiment, the plot shown in Fig. 1 produces a straight line and its slope gives the respective rate constant of propagation. This slope, calculated by the least square method, leads to a value of 550 l. moles<sup>-1</sup> sec.<sup>-1</sup>, and on assumption that the line must go through the origin, a least square value of 548 is obtained. The agreement between both values shows that the time of

"killing" and the time of mixing are negligible if compared with the time of reaction.

The method described here demonstrates that the rate of propagation is first order in monomer at least over a concentration range of 0.02–0.22 *M*. On the other hand, it is found that the rate of propagation is a more complex function of the concentration of "living" ends since the calculated rate constant decreases with increasing concentration of the growing ends (see Table II). Presumably, either the association of the "living" ends decreases their reactivity, or the reactivity is a function of environment, *e.g.*, of ionic strength of the solution. We feel that the latter point of view is probably more nearly correct; however, further work is required to clarify this issue. Variations in the propagation rate constant resulting from changes of counterions and of solvent are under investigation.

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### ONE STEP OXIDATION OF THALLIUM(I) TO THALLIUM(III)<sup>1</sup>

Sir:

A preliminary report of our investigation of the oxidation of Tl(I) by Ce(IV) in 6.18 *f* HNO<sub>3</sub> at 53.9° is presented here because the results

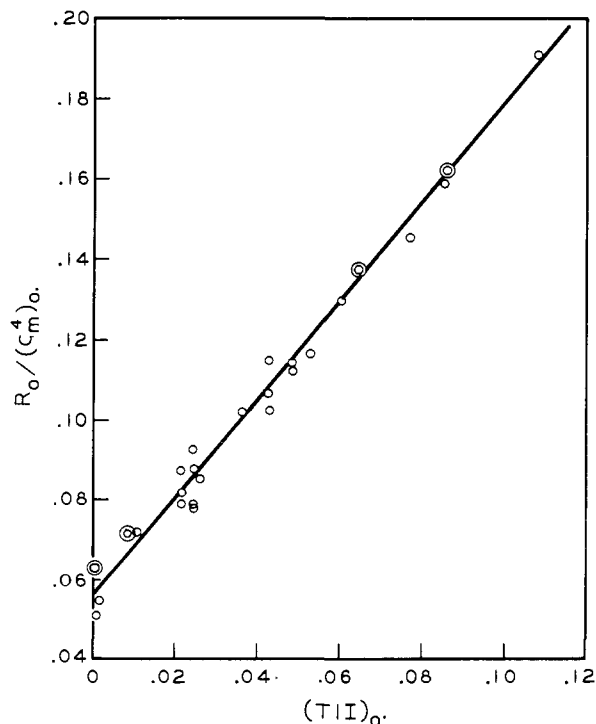


Fig. 1.—Comparison of empirical rate law with experiments:  $R_0$  is initial rate;  $(\text{TlI})_0$  is initial Tl(I) concentration;  $(C_m^4)_0$  is initial concentration of Ce(IV) monomer.

can be used to prove that a two electron transfer occurs, perhaps by oxygen atom transfer, in some

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oxidations of Tl(I). Whether or not such two electron oxidations occur for metal-ions has been the object of much discussion.<sup>2</sup>

The procedure used for following the reaction depended upon the initial concentration of reactants. In some experiments Ce(IV) was determined by titration with ferrous sulfate, in others Ce(IV) was determined spectrophotometrically, and in others radioactive Tl(III) was determined after an extraction of Tl(III) into tributyl phosphate. For the last procedure, radioactive Tl(I) and Tl(III) in isotopic equilibrium were used in the reaction mixture and a correction was made for a small extraction of Tl(I). Light was excluded from the reaction mixtures. Chemicals from different lots and from more than one manufacturer were used for each reagent. The thallium and cerium reagents were purified further. Several sources of distilled water were used, with and without additional chemical treatment and distillation. Freshly boiled HNO<sub>3</sub> and HNO<sub>3</sub> direct from reagent bottles were employed. The rate of reaction was insensitive to these variables. The reaction was stoichiometric to within experimental error.

The initial slopes of graphs of (Tl(III)) *vs.* time for over 50 experiments in which (Ce(IV)) varied from 0.00190 to 0.2274 *f*, (Tl(I)) varied from 0.0032 to 0.1074 *f*, (Ce(III)) varied from 0.0 to 0.1560 *f*, and (Tl(III)) varied from 0.0 to 0.1140 *f* are in agreement with an empirical rate law which, in the absence of (Ce(III)), has the form

$$R = \frac{d(\text{Tl(III)})}{dt} = k(\text{Ce(IV)}) + k'(\text{Ce(IV)})(\text{Tl(I)})$$

where  $k$  and  $k'$  are constants and (Ce(IV)) is the concentration of monomeric<sup>3</sup> Ce(IV). Figure 1 shows the agreement between the empirical rate law and the experimental rates when a value of 20 is used for the dimerization constant of Ce(IV). The value of  $k$  determined from the intercept of the graph is 0.056 h.<sup>-1</sup> and the value of  $k'$  is 1.23 l. m.<sup>-1</sup> h.<sup>-1</sup>.

In the presence of Ce(III) the rate of the reaction is inhibited markedly. Thallium(III) has no effect on the rate. The first term in the empirical rate law requires a mechanism involving an intermediate formed by a reaction of Ce(IV). This intermediate cannot contain thallium. In order to account for the inhibition by Ce(III), competition between Ce(III) and Tl(I) for the intermediate must be invoked. Assuming that the precautions taken to eliminate the necessity for considering impurities were successful, we conclude that the only possible reacting substances are H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup>. Reasonable intermediates would be OH or NO<sub>3</sub>. The reaction between Tl(I) and the intermediate must be either a one-electron transfer to give Tl(II) and the original compound from which the intermediate was formed or a two electron

(2) (a) J. Halpern, *Can. J. Chem.*, **37**, 148 (1959); (b) W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 447 (1957); (c) F. H. Westheimer in "The Mechanism of Enzyme Action," edited by W. D. McElroy and H. B. Glass, The Johns Hopkins University Press, Baltimore, Md., 1954, pp. 321-352.

(3) B. D. Blaustein and J. W. Gryder, *J. Am. Chem. Soc.*, **79**, 540 (1957).