

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

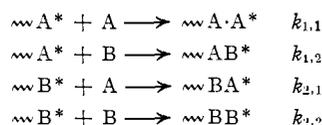
## The Absolute Rate Constants of Anionic Co-polymerization in the System Styrene- $\alpha$ -Methylstyrene. The Effect of Polymer Structure on the Rate of Polymerization

BY D. N. BHATTACHARYYA, C. L. LEE, J. SMID AND M. SZWARC

RECEIVED MAY 10, 1962

The lack of termination in anionic polymerization permits one to determine directly the absolute rate constants of anionic co-polymerization. A capillary flow technique suitable for this purpose has been described. The systems investigated here involved: living poly- $\alpha$ -methylstyrene + styrene and living polystyrene +  $\alpha$ - or  $\beta$ -methylstyrene. It was shown that the rate of addition of styrene to  $\alpha$ -methylstyrene<sup>-</sup> ion depends on the counter-ion and on the structure of the polymer. In particular, the nature of the penultimate unit, the type of linkage between the last unit and the penultimate unit and the size of polymeric molecule were shown to be factors influencing the rate constant of copolymerization.

The copolymerization of two monomers A and B involves four propagation steps, *i.e.*



The star used in these equations represents a growing chain and  $k_{1,1}$ ,  $k_{1,2}$ , etc., denote the respective rate constants which are assumed to be independent of the nature of the preceding units and the type of their linkage. The success of this scheme in accounting for the numerous results of radical copolymerization provides perhaps the best argument for its validity (see the recent review of this field in Walling's monograph "Free Radicals in Solution").

The assumption that  $k_{1,1}$ ,  $k_{1,2}$ , etc., are independent of the character of the preceding units is only a first approximation, and it was realized<sup>1</sup> that for some systems a more elaborated treatment<sup>2</sup> might be required. In fact, systems have been reported<sup>3,4</sup> in which the effect of penultimate units upon the rate of growth is significant.

The common technique used in studies of copolymerization kinetics is based on the relation that exists between the composition of the copolymer and of the feed.<sup>1</sup> This method, although satisfactory for radical copolymerization, might fail in other systems, *e.g.*, in anionic copolymerization.<sup>5</sup> It is desirable, therefore, to develop alternative techniques for determining the copolymerization rate constants in anionic polymerization. A novel technique useful for such a study is described in the present paper. This method is suitable for determining the absolute values of the rate constants of anionic copolymerization, while only their ratios could be determined by the conventional method. It has the added advantage that it permits the direct investigation of the influence of the preceding units and of their mode of linkage upon the rate constants of propagation.

**The Method of Attack.**—Under suitable conditions anionic polymerization may proceed without termination. The resulting polymer, referred to as a "living" polymer,<sup>6</sup> retains its ability to grow at least for the time required to complete the experiment. The addition of a monomer to a solution of such polymers initiates further polymerization which may be followed by any suitable method. Since the concentration of growing ends can be determined, the results lead to the absolute values of the respective rate constants.

(1) T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952.

(2) E. Mertz, T. Alfrey and G. Goldfinger, *J. Polymer Sci.*, **1**, 75 (1946).

(3) W. G. Barb, *ibid.*, **11**, 117 (1953).

(4) G. E. Ham, *ibid.*, **45**, 169 (1960).

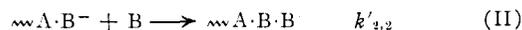
(5) R. K. Graham, D. L. Dunkelberger and W. E. Goode, *J. Am. Chem. Soc.*, **82**, 400 (1960).

(6) (a) M. Szwarc, M. Levy and R. Milkovitch, *ibid.*, **78**, 2656 (1956); (b) M. Szwarc, *Nature*, **178**, 1168 (1956).

The addition of a monomer B to a solution of living polymers possessing terminal A units leads to<sup>7</sup> the reaction



This reaction is then followed by reactions II and III which represent the homo-polymerization of the monomer B



The experiments are carried out under conditions which minimize the extent of the latter reactions. This is achieved by having *higher* concentrations of  $\sim\sim A^-$  than that of the monomer B, and by extrapolating the results to zero conversion, *i.e.*, by shortening the time of the reaction. Thus, the rate constant of copolymerization,  $k_{1,2}$ , is determined by the initial rate of reaction.

**Mathematical Treatment of the Problem.**—In the absence of termination the kinetics of the polymerization described by the equations I, II and III is given by the differential equations

$$-d[\sim\sim A^-]/dt = k_{1,2}[\sim\sim A^-][B] \quad (1)$$

$$-d[B]/dt = \{k_{1,2}[\sim\sim A^-] + k_{2,2}[\sim\sim AB_n^-]\}[B] \quad (2)$$

in which we assume, for mathematical simplicity, that  $k'_{2,2} = k_{2,2}$ . This simplification is permissible, since we shall be only concerned with the cases where the extent of homopropagation of the monomer B is negligible.

A general solution of these equations is complicated. However, the results may be simplified if  $k_{1,2}[\sim\sim A^-] \gg k_{2,2}[\sim\sim AB_n^-]$  or if  $k_{1,2} \approx k_{2,2}$ . In the former case, the equations are reduced to

$$-d[B]/dt = k_{1,2}[\sim\sim A^-][B] \quad (3)$$

where

$$[\sim\sim A^-] = [\sim\sim A^-]_0 - ([B]_0 - [B])$$

If the decrease in the monomer concentration  $[B]_0 - [B]$  is denoted by  $x$ , then equation 3 may be rewritten in the conventional form for a bimolecular process, *i.e.*

$$-dx/dt = k_{1,2}(A_0 - x)(B_0 - x) \quad (4)$$

Hence, a plot of  $(A_0 - B_0)^{-1} \ln \{B_0(A_0 - x)/A_0(B_0 - x)\}$  versus time should result in a straight line with a slope equal to  $k_{1,2}$ , for a sufficiently short time interval.

In the second case when  $k_{1,2} \approx k_{2,2}$  one may rewrite equation 2 in the form

$$-d[B]/dt = k_{1,2}[\sim\sim A^-]_0[B] + (k_{2,2} - k_{1,2})[\sim\sim AB_n^-][B] \quad (5)$$

and for the initial stages of the polymerization, (5) is reduced to the conventional equation describing a first order reaction

$$-d[B]/dt \approx k_{1,2}[\sim\sim A^-]_0[B] \quad (6)$$

The validity of this approximation is further strengthened if  $[\sim\sim A^-]_0 > [B]_0$ . Hence, for  $(k_{1,2} - k_{2,2}) \ll k_{1,2}$  and  $[\sim\sim A^-]_0 > [B]_0$  the plot of  $-(\ln [B])/[\sim\sim A^-]_0$

(7) For the sake of brevity the growing species are represented as anions. In most systems we deal, however, with ion-pairs, *e.g.*  $\sim\sim A^-, Na^+$ .

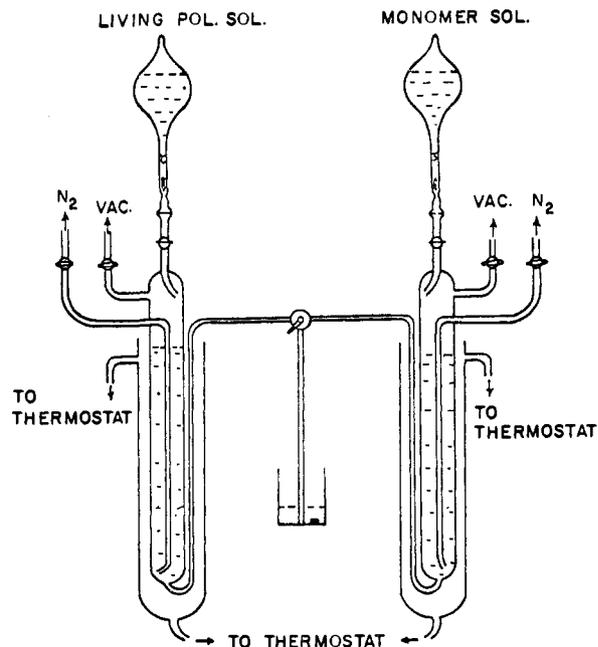


Fig. 1.—Flow apparatus for measuring rates of fast reactions.

versus time should give a straight line, at least for the initial stages of the process, with a slope equal to  $k_{1,2}$ . It should be stressed at this place that both graphic methods give essentially the same value of  $k_{1,2}$  if  $[\sim A^-]_0 > [B]_0$  and the conversion of B is not greater than 20 or 30%.

If  $k_{2,2} \gg k_{1,2}$  the explicit solution of equations 1 and 2 becomes complicated. In this case, however, the ratio  $k_{1,2}/k_{2,2}$  may be calculated if the concentration of  $\sim A^-$  is determined at the end of the reaction. Examples of such kinetics are given in a forthcoming paper.

### Experimental

A capillary flow technique suitable for studies of fast anionic polymerizations was described in a previous paper.<sup>8</sup> The polymerization ensued when a solution of living polymer, of a known concentration of growing ends, was mixed with a monomer solution in the plug of a three-way stopcock (see Fig. 1). The mixture flowed through a vertical capillary into a beaker containing wet solvent which instantly terminated the polymerization. The amount of the unreacted monomer was then determined and the percentage of conversion calculated. The time of polymerization could be calculated from the rate of flow through the vertical capillary, and hence all the data necessary to determine the absolute rate constant of propagation were available. The small volume of the vertical capillary allowed us to shorten the time of reaction to as little as 0.05 sec., and therefore the initial stages of polymerization could be investigated.

All the living oligomers and polymers were prepared in tetrahydrofuran solution in all-glass equipment on a high vacuum line. The di-sodium salt of  $\alpha$ -methylstyrene tetramer and di-potassium salt of  $\alpha$ -methylstyrene dimer and tetramer were prepared by treating the tetrahydrofuran solution of the purified monomer with sodium and potassium metal, respectively. A detailed account of these preparations is given elsewhere.<sup>9</sup> Cumylpotassium was prepared from cumyl ether,  $\text{PhC}(\text{CH}_3)_2\text{OCH}_3$ , by the Ziegler method.<sup>10</sup> The conversion into cumylpotassium was quantitative and the insoluble potassium methoxide was removed by filtering the solution through a sintered glass plate. The details of the preparation of living polystyrene solution are described elsewhere.<sup>8b</sup>

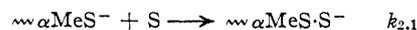
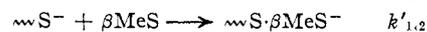
The solutions of living polymers or oligomers were transferred into evacuated glass ampoules equipped with breakseals and used, if possible, on the same day. If the experiment was delayed, the ampoules were stored in a deep-freezer, and used after a day or two at the most. The concentration of living ends in an investigated solution was determined by titrating aliquots with methyl iodide.<sup>8b</sup>

The rigorously purified monomer solutions were transferred to similar glass ampoules and their concentrations determined by spectrophotometric analysis of aliquots. The results of these analyses were compared with the concentrations calculated from the original composition of the solution, and in a satisfactory preparation the agreement was within 2%.

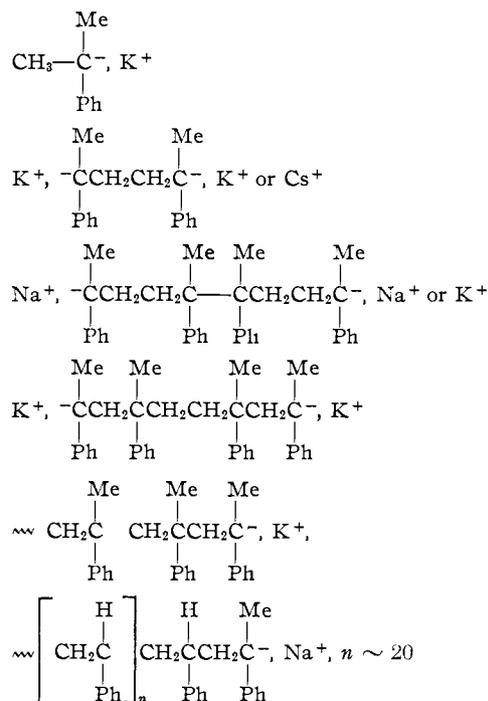
Two ampoules, one containing the living polymer and another filled with the monomer solution, were sealed to the flow apparatus shown in Fig. 1. After evacuation of the system the solutions were introduced into the reservoirs by crashing the breakseals of the ampoules. A series of experiments then were performed, the time of flow being changed in each experiment by varying the pressure of the nitrogen which was used to press the solution into the stopcock. The "killed" solution was collected in the beaker and analyzed spectrophotometrically or by gas chromatography for the unreacted monomer. A detailed account of this technique is given in the previous paper<sup>8b</sup> to which the reader is referred for further information.

### Results

These systems were investigated



where S denotes a styrene unit while  $\alpha \text{MeS}$  and  $\beta \text{MeS}$  represent  $\alpha$ - and  $\beta$ -methylstyrene, respectively. The last reaction, *i.e.*, the addition of styrene to  $\sim \alpha \text{MeS}^-$ , was carried out with a variety of living polymers, all possessing the same terminal  $\alpha \text{MeS}^-$  units but differing in the nature of the preceding units, molecular weight, type of linkage and the counter-ion, *i.e.*



These studies, therefore, shed light on the effect which all these factors exert on the rate constant of copolymerization (compare, *e.g.*, Tables I with IV, and I with II and III).

All the investigated polymerizations were carried out in tetrahydrofuran solution at 25°. No attempt was made to determine the respective activation energies, but it was noticed that they are low. Indeed, under these conditions, the homopropagation of styrene proceeds with  $E \sim 1$  kcal./mole,<sup>8b</sup> and that of  $\alpha$ -methylstyrene shows  $E \sim 2-3$  kcal./mole.<sup>11</sup>

All the experimental data and the respective rate constants are given in Tables I through V. The second approximation, as outlined in the preceding section, was applied when treating the kinetics of styrene addition to  $\alpha$ -methylstyrene<sup>-</sup> end groups; *i.e.*, this copoly-

(8) (a) C. Geacintov, J. Smid and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 1253 (1961); (b) C. Geacintov, J. Smid and M. Szwarc, *ibid.*, **84**, 2508 (1962).

(9) C. L. Lee, J. Smid and M. Szwarc, *J. Phys. Chem.*, **66**, 904 (1962).

(10) K. Ziegler and H. Dislich, *Ber.*, **90**, 1107 (1957).

(11) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **36**, 1141 (1958).

TABLE I

Rate constant of styrene addition to disodium and dipotassium salts of  $\alpha$ -methylstyrene tetramer in tetrahydrofuran at 25°. The data are treated as a first order reaction, and the rate constants calculated for a plug flow (Method I).

Counter ion	Concn. of living ends $\times 10^3 M$	Initial concn. of styrene $\times 10^3 M$	% Conversion	$k_{2,1}$ , 1. mole <sup>-1</sup> sec. <sup>-1</sup>
Na <sup>+</sup>	1.3	1.0	12-22	1070
Na <sup>+</sup>	1.3	1.1	11-23	1010
Na <sup>+</sup>	1.3	1.1	11-24	990
Na <sup>+</sup>	2.2	0.8	15-25	890
Na <sup>+</sup>	2.3	0.8	9-25	885
Na <sup>+</sup>	3.0	2.2	20-39	780
Na <sup>+</sup>	3.0	2.6	20-32	780
Na <sup>+</sup>	3.5	3.0	21-41	780
Na <sup>+</sup>	4.0	2.0	20-45	665
Na <sup>+</sup>	4.0	3.0	10-31	660
Na <sup>+</sup>	4.3	2.5	18-35	540
Na <sup>+</sup>	5.2	4.0	16-37	585
Na <sup>+</sup>	5.4	3.0	10-38	610
Na <sup>+</sup>	7.0	3.0	35-70	645
Na <sup>+</sup>	7.3	2.6	31-47	565
Na <sup>+</sup>	9.5	5.5	45-60	660
Na <sup>+</sup>	13.0	3.0	54-73	640
K <sup>+</sup>	1.9	1.2	16-33	1050
K <sup>+</sup>	2.6	2.7	6-21	950
K <sup>+</sup>	3.8	1.5	21-45	840
K <sup>+</sup>	10.0	5.5	52-65	700

TABLE II

Rate constant of styrene addition to dipotassium and disodium salts of  $\alpha$ -methylstyrene dimer in tetrahydrofuran at 25°. The data are treated as a first order reaction and the rate constants calculated for a plug flow (Method I).

Counter ion	Concn. of living ends $\times 10^3 M$	Initial concn. of styrene $\times 10^3 M$	% Conversion	$k_{2,1}$ , 1. mole <sup>-1</sup> sec. <sup>-1</sup>
K <sup>+</sup>	3.5	1.8	29-44	1280
K <sup>+</sup>	5.4	3.0	40-78	1180
K <sup>+</sup>	8.5	1.9	58-76	1180
Cs <sup>+</sup>	3.0	2.9	43-65	880
Cs <sup>+</sup>	3.5	2.6	41-72	826
Cs <sup>+</sup>	4.0	2.9	35-54	530

TABLE III

Rate constant of styrene addition to potassium salt of cumene in tetrahydrofuran at 25°. The data are treated as a second order reaction, and the rate constant calculated for a plug flow.<sup>a</sup>

Concn. of living ends $\times 10^3 M$	Initial concn. of styrene $\times 10^3 M$	% Conversion	$k_{2,1}$ , 1. mole <sup>-1</sup> sec. <sup>-1</sup>
3.0	2.6	41-57	3100
4.2	1.5	70-91	4130

<sup>a</sup> The calculation based on the first order reaction gives a curve instead of a straight line, while a straight line is obtained in the second order plot. This is consistent with the fact that in this system  $k_{2,1} \gg k_{1,1}$ .

merization was treated as a first order reaction. The addition of  $\alpha$ - and  $\beta$ -methylstyrene to living polystyrene was treated as a second order reaction; *i.e.*, the first approximation was used in calculations. The reproducibility of the experiments, and the validity of the applied approximations, is illustrated by Fig. 2 (for the first order kinetics) and by Fig. 3 (for the second order kinetics).

The addition of styrene to the terminal  $\alpha$ -Me-styrene<sup>-</sup> units proceeds very fast; therefore the respective experiments had to be performed at very high rates of flow causing its turbulence. Consequently, the respective rate constants were calculated on the basis of the kinetic equations derived for a plug flow, as de-

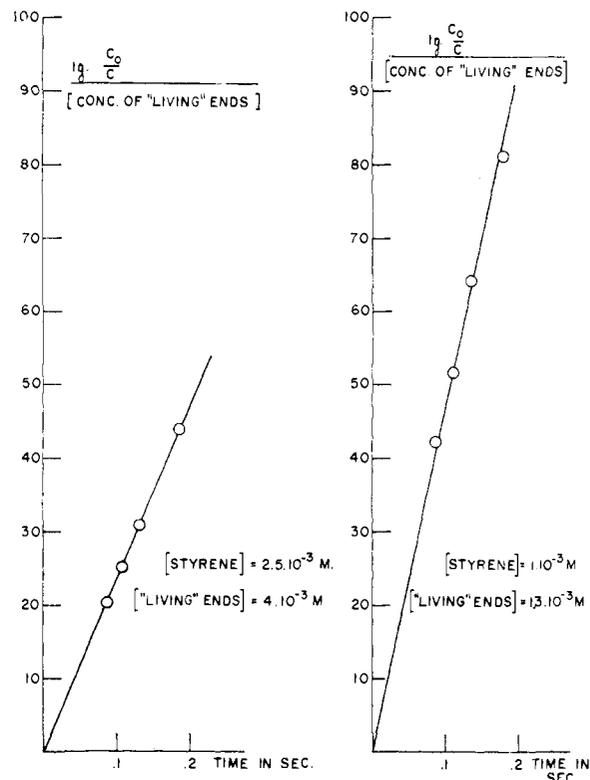


Fig. 2.—Copolymerization of styrene with living  $\alpha$ -methylstyrene tetramer in THF at 25°.

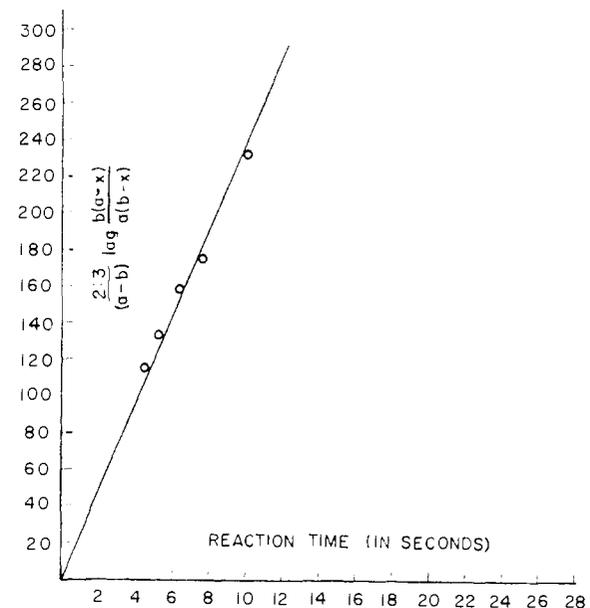


Fig. 3.—Copolymerization rate constant of  $\alpha$ -methylstyrene and living polystyrene at 25°.

scribed in ref. 8b (Method I of calculations). On the other hand, a relatively slow flow was maintained in the experiments involving the addition of  $\alpha$ - or  $\beta$ -methylstyrene to living polystyrene. Such a flow may be laminary, and then computations have to be carried out by a modified method as described in the Appendix. In fact, both methods, *i.e.*, Method I (plug flow) and Method II (laminary flow) were used in calculations, and the respective results are given in Table V. Fortunately, the resulting  $k_{1,2}$ 's differ by 25% only.

Discussion

The data presented in Tables I through IV show that the rate constants of the styrene addition to ter-

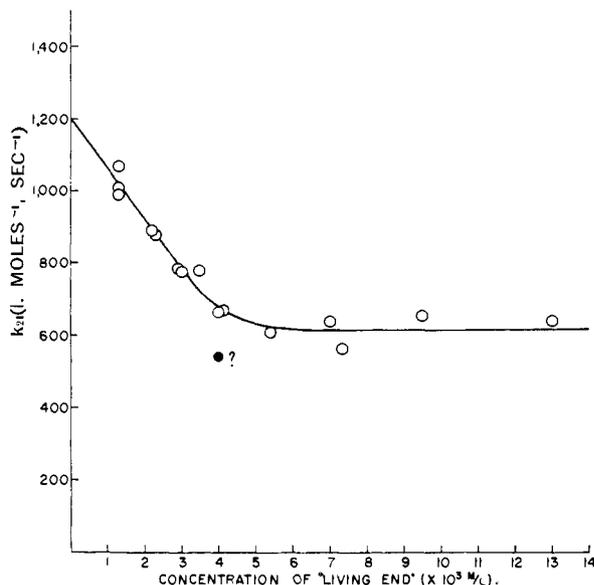
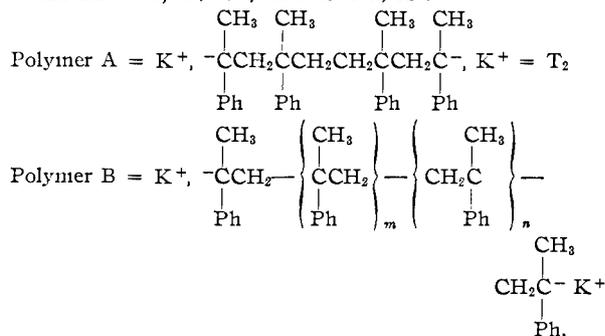


Fig. 4.—Dependence of  $k_{2,1}$  on concentration of "living end."

terminal  $\alpha$ -methylstyrene<sup>-</sup> units are affected by the nature of the counter-ion and of the penultimate unit and by the structure of the polymer. Moreover, it seems that the values of  $k_{2,1}$  for a particular system, increase with decreasing concentration of living ends as shown by the data listed in the tables and as illustrated by Fig. 4. The plateau shown in Fig. 4 is significant, suggesting some saturation effect. The same behavior was reported earlier for the anionic homo-polymerization of styrene in tetrahydrofuran<sup>8</sup> and a similar concentration dependence was observed for other systems investigated in this Laboratory. A tentative explanation of this phenomenon is given in ref. 8b, but further studies are desirable. In two series of experiments it was demonstrated that the addition of a ten-fold excess of sodium

TABLE IV

Addition of styrene to poly- $\alpha$ -methylstyrenes in tetrahydrofuran, the penultimate unit linked in a head-to-tail fashion to the last unit;  $T$ , 25°; counter-ion,  $K^+$ .



Type of polymer	Concn. living ends, $\times 10^3 M$	Init. concn. of styrene, $\times 10^3 M$	% Conversion	$k_{2,1}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
A	4.25	3.1	40-67	141
B; $n \sim 2$	4.0	3.1	36-67	137

Rate constant of styrene addition to di-sodium salt of poly-styrene possessing one unit of  $\alpha$ -methylstyrene at each living end linked in a head-to-tail fashion

Concn. of living ends $\times 10^3 M$	Init. concn. of styrene $\times 10^3 M$	% Conversion	$k_{2,1}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup>
2.3	1.5	41-61	2100
2.6	2.6	30-61	1840
3.3	2.6	34-54	1700
3.8	2.7	28-46	1470

TABLE V

Rate constant of  $\alpha$ -methylstyrene addition to living polystyrene: Treated as a second order reaction; solvent tetrahydrofuran; counter-ion  $Na^+$ ;  $T$ , 25°.

Concn. of living ends $\times 10^3 M$	Init. concn. of $\alpha$ -Me-styrene $\times 10^3 M$	% Conversion of the monomer	$k_{1,2}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup> Method I	Method II
2.5	4.5	20-33	27.0	32.9
4.3	4.9	30-57	23.2	29.2
7.4	7.7	53-64	23.9	30.4

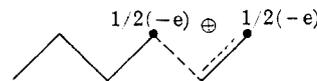
Rate constant of  $\beta$ -methylstyrene addition to living polystyrene: Solvent, tetrahydrofuran; counter-ion,  $Na^+$ ;  $T = 25^\circ$

Concn. of living end $\times 10^3 M$	Init. concn. of $\beta$ -Me-styrene $\times 10^3 M$	% Conversion of the monomer	$k_{1,2}$ , l. mole <sup>-1</sup> sec. <sup>-1</sup> Method I	Method II
5.5	8.5	29-46	17.6	21.8
5.3	6.4	35-52	18.0	21.4

perchlorate to the living sodium tetramer of  $\alpha$ -methylstyrene had no effect on the rate of its copolymerization with styrene. A similar observation was reported for the anionic homo-polymerization of styrene.<sup>8b</sup> The reason for this behavior has been elucidated recently, and the pertinent discussion will be reported in a forthcoming publication.

The effect of counter-ions on the rate of copolymerization is shown by the data listed in Tables I and II. Polymers associated with  $Cs^+$  grow more slowly than those possessing  $K^+$  counter-ions. This trend was observed for the homo-polymerization of styrene<sup>12</sup>—the rate of propagation decreasing along the series  $Li^+ > Na^+ > K^+ > Cs^+$ . On the other hand, the comparison of  $Na^+$  and  $K^+$  seems to be confusing. Actually, the data presented in Table I seem to indicate that for the same concentration of the growing ends the di-potassium salt of  $\alpha$ -methylstyrene tetramer reacts slightly faster than the sodium salt. This observation may be misleading since it is impossible to prepare the potassium salt of  $\alpha$ -methylstyrene tetramer without contaminating it with some amount of the dimer.<sup>9</sup> The dimer is more reactive than the tetramer and its presence in the potassium salt may account for the observed discrepancy.

The following explanation may account for the observed counter-ion effect. Let us assume that in the transition state the counter-ion is located between the last unit of the polymer and the new one which is being added, as



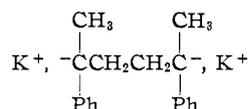
Its increasing size interferes then with the monomer's approach, making the incipient C-C bond longer, the activation energy of the process higher, and the rate constant lower.

The structural factors affecting the rate of addition of styrene to  $\alpha$ -methylstyrene<sup>-</sup> ions seem to be steric in nature. The addition to cumene<sup>-</sup>,  $K^+$  (see Table III) is undoubtedly the fastest, the addition to  $\alpha$ -methylstyrene<sup>-</sup> unit preceded by styrene units (see Table IV) is somewhat slower, and the addition to poly- $\alpha$ -methylstyrene possessing the terminal head-to-tail units (see Table IV) is by far the slowest. The rates of addition to the  $\alpha$ -methylstyrene dimer or tetramer, in which all

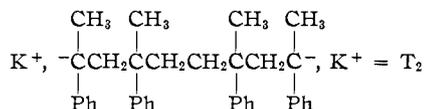
(12) (a) M. Szwarc, "Advances in Chemistry Series," No. 34, 1962, p. 96; (b) J. Smid and M. Szwarc, *J. Polymer Sci.*, **61**, 37 (1962).

the units are presumably linked in a head-to-head or tail-to-tail fashion, are faster than the addition to the head-to-tail linked poly- $\alpha$ -methylstyrenes, although they are still slower than the other additions.

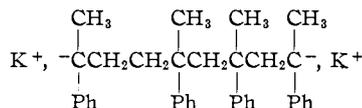
The reactions involving the head-to-tail linked poly- $\alpha$ -methylstyrenes need further consideration. These polymers were prepared from the di-potassium salt of  $\alpha$ -methylstyrene dimer by adding to it desirable amounts of  $\alpha$ -methylstyrene. The polymer A (see Table IV) was formed by adding an amount of monomer sufficient to polymerize two molecules of  $\alpha$ -methylstyrene with each dimer. (Of course, more than two equivalents had to be added to achieve such a result, since a fraction of the monomer remains in solution in equilibrium with the living polymer, see *e.g.*, the paper by Vrancken, Smid and Szwarc.<sup>13</sup>) The polymer B (see Table IV) was prepared by adding twenty equivalents of the monomer to the dimer, thus producing a longer chain of head-to-tail linked units. The structure of the dimer was established<sup>9,14</sup> as



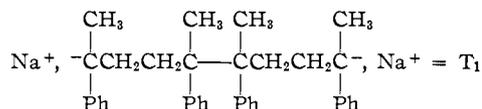
The tetramer A = T<sub>2</sub> should therefore have the structure



although it may also contain a small amount of



On the other hand, the tetramer T<sub>1</sub> produced directly from the monomer was shown to have the structure<sup>9,13</sup>



The fact that the former tetramer is considerably less reactive than the latter proves that these two oligomers are different, thus confirming indirectly the proposed structure of T<sub>1</sub>. A similar argument, based on equilibrium studies, was used in the previous communications.<sup>9,13</sup> It should be stressed that the difference in the reactivities of those two tetramers is too large to be attributed to the change of the counter-ion and arises from the different linkage (*i.e.*, head-to-head in T<sub>1</sub> and head-to-tail in T<sub>2</sub>). It was also checked that the presence of free  $\alpha$ -methylstyrene affects only slightly the rate of addition of styrene to the living T<sub>1</sub>  $\alpha$ -methylstyrene tetramer. In these experiments, the rate constant of styrene addition to a solution of tetramer T<sub>1</sub> was determined twice: in absence of  $\alpha$ -methylstyrene monomer and in the presence of about  $3 \times 10^{-2}$  M concentration of  $\alpha$ -methylstyrene, *i.e.*, an amount which exceeds the concentration of styrene by about a factor of ten. In twice repeated experiments the observed rate constant of addition decreased only by about 20% on  $\alpha$ -methylstyrene addition. It was calculated from the data of Vrancken, *et al.*,<sup>13</sup> that at this concentration and at 25° only a negligible fraction of tetramer is converted into pentamer. These experiments showed that the presence of free  $\alpha$ -methylstyrene

in the solution of T<sub>2</sub> tetramer or the polymer were not responsible for the low rate constant of addition.

It is interesting to notice that further addition of  $\alpha$ -methylstyrene to the head-to-tail linked tetramer does not affect its reactivity (see Table IV). This observation parallels that made during the studies of equilibria between oligomers and polymers of  $\alpha$ -methylstyrene and their monomer.<sup>13</sup> The equilibrium constant was found to be larger for the addition to the head-to-head linked terminal units than for the head-to-tail linked ones, and in the latter case, further increase in the length of the chain had no effect upon the equilibrium constant.

Finally, attention should be drawn to the fact that the rate of addition to the dimer is greater than to the head-to-head-tail-to-tail linked tetramer, in spite of the fact that these two polymers possess identical terminal and penultimate units. This observation parallels again that made in the course of the equilibrium studies.<sup>13</sup> Two interpretations may be suggested for these results: either the electrostatic repulsion between the neighboring ends of the dimer contributes to the free energy and activation energy of the process, or the binding of two dimers into tetramer affects the steric requirements of their terminal units, as is indeed shown by the models. We prefer the latter interpretation, since the rate of addition to cumene potassium was found to be extremely large, and of course no electrostatic repulsion may be invoked in this case.

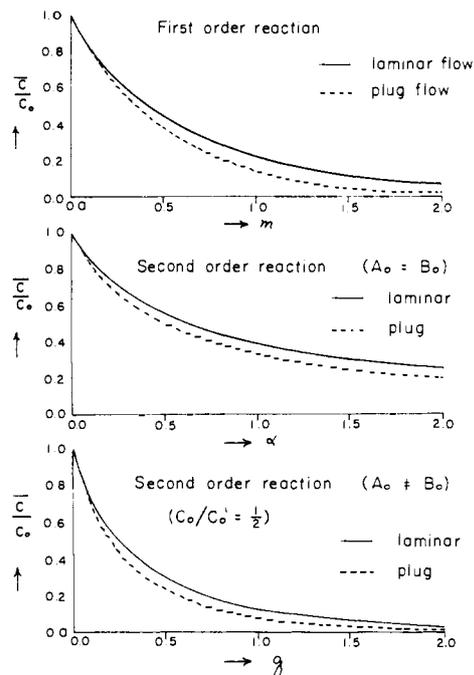


Fig. 5.—Comparison of laminar and plug flow.

The addition of  $\alpha$ -methylstyrene to living polystyrene obeys second order kinetics, since the rate constant of  $\alpha$ -methylstyrene homopolymerization turns out to be much slower than the rate constant of copolymerization (the case  $k_{1,2} \gg k_{2,2}$ ). The pertinent results are given in Table V and the course of the reaction is illustrated by Fig. 3. The substantially lower value of  $k_{1,2}$ , when compared with  $k_{2,1}$ , indicates the effect of electron-donating methyl substituent which enhances the addition of styrene to poly- $\alpha$ -methylstyrene<sup>-</sup> ion but hinders the addition of  $\alpha$ -methylstyrene to polystyrene<sup>-</sup> ion. It may be assumed that the steric hindrance is similar for both reactions. The homopolymerization of  $\alpha$ -methylstyrene corresponds to a still

(13) A. Vrancken, J. Smid and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2036 (1962).

(14) C. F. Frank, *et al.*, *J. Org. Chem.*, **26**, 307 (1961).

lower rate constant ( $k_{2,2} \sim 2.5$  (l./mole sec.<sup>-1</sup>) at 25°, extrapolated from the data of Worsfold and Bywater<sup>11</sup>), the low activity undoubtedly being due to the considerable steric hindrance.

The addition of  $\beta$ -methylstyrene to living polystyrene proceeds again as a second order reaction, demonstrating the reluctance of  $\beta$ -methylstyrene to homo-polymerize. The results are also given in Table V, and show that the addition of this monomer is only slightly slower than the addition of  $\alpha$ -methylstyrene. This is rather a surprising result, since it was expected that the  $\beta$ -substituent would substantially hinder the polymerization.

The reaction of  $\beta$ -methylstyrene involves a complicating factor arising from the presence of reactive hydrogen atoms of the  $\beta$ -methyl group. The proton abstraction from such a group gives a very stable allyl<sup>-</sup> ion conjugated with a phenyl group. Thus, the benzyl<sup>-</sup> ions are transformed into these stable ions and the occurrence of such a process is manifested by the change of the absorption spectrum of the solution (see, e.g., a paper by Spach, Levy, and Szwarc<sup>15</sup> describing a similar process in the polystyrene system).

In conclusion, we wish to acknowledge the financial support of these studies by the National Science Foundation through Grant No. G-14393.

### Appendix

Kinetics of reactions taking place in a plug flow are described by the conventional equations in which the residence time  $\tau$  gives the duration of the process,  $\tau$  being the ratio (reactor's volume)/(rate of flow). Such expressions approximately apply to kinetics of processes taking place in a turbulent flow. However, this approximation is unsatisfactory for a reaction proceeding in a laminary flow. Under such conditions, the volume elements located at different distances from the axis of the tube spend different time in the reactor. Consequently, the degree of conversion in each volume element is a function of  $r$ , where  $r$  is the distance of the element from the axis of the tube. The average concentration of a product at the outlet of the tube is then given by the integral

$$\bar{C} = \int_0^R 2\pi r u c_r dr / \pi R^2 \bar{u}$$

where  $u$  and  $c_r$  are the velocity and concentration in a lamina at the distance  $r$  from the axis of the tube,  $R$  is the radius of the tube and  $\bar{u}$  the average velocity of the liquid.

In a laminary flow the gradient of velocity  $du/dr$  is given by the equation

$$-du/dr = pr/2\eta$$

where  $p$  is the pressure gradient (assumed to be constant along the whole length of the tube) and  $\eta$  the viscosity of the liquid is also assumed to be constant. Hence

$$u = (p/4\eta)(R^2 - r^2) = 2\bar{u}(1 - r^2/R^2)$$

and the time of residence  $\tau$  in a capillary of length  $L$  and volume  $V$  is

$$\tau = 8V\eta/\pi R^4 p = L/\bar{u}$$

For a second order reaction where  $A_0 = B_0$ ,  $C_r$  at the outlet of the tube is given by

$$C_r = \{k_2 L/u_r + 1/C_0\}^{-1}$$

and the integration gives

$$\bar{C}/C_0 = 1 - \alpha + 2\alpha^2 \ln(1 + \alpha^{-1})$$

where  $\alpha = (1/2)k_2 C_0 \tau$ . Values of  $\bar{C}/C_0$  for different  $\alpha$ 's are given in Table VI, and this permits the calculation of  $\alpha$  for any  $\bar{C}/C_0$ . A plot of  $\alpha/C_0$  versus  $\tau$  should result in a straight line having a slope of  $(1/2)k_2$ , and thus  $k_2$  may be determined from experimental results.

For a second order reaction for which  $A_0 = C_0$  and  $B_0 = C_0'$ , we find

$$-dC_r/dt = k_3 C_r (C_0' - C_0 + C_r)$$

Hence

$$C_r = C_0(C_0' - C_0) / \{C_0' \exp[k_3(C_0' - C_0)L/u_r] - C_0\}$$

and

$$\bar{C}/C_0 = 2(1 - C_0/C_0') \int_0^1 \frac{x dx}{\exp(g/x) - C_0/C_0'}$$

where  $g = (1/2)k_3(C_0' - C_0)\tau$ .

In Table VII the values of  $\bar{C}/C_0$  are tabulated as functions of  $g$

TABLE VI

VALUES OF THE AUXILIARY VARIABLE  $\alpha$  NEEDED FOR THE CALCULATION OF THE BIMOLECULAR RATE CONSTANT ( $A_0 = B_0$ ) IN A FLOW TECHNIQUE FOR A LAMINARY FLOW

$\alpha$	$\bar{C}/C_0$	$\alpha$	$\bar{C}/C_0$	$\alpha$	$\bar{C}/C_0$
0.000	1.0000	0.70	0.4664	2.60	0.1997
.025	0.9546	0.80	.4380	2.80	.1877
.050	.9152	0.90	.4105	3.00	.1782
.075	.8800	1.00	.3863	3.50	.1571
.10	.8480	1.20	.3457	4.00	.1405
.15	.7917	1.40	.3129	4.50	.1272
.20	.7433	1.60	.2858	5.00	.1160
.30	.6639	1.80	.2630	6.00	.1010
.40	.6009	2.00	.2438	7.00	.0810
.50	.5493	2.20	.2269	8.00	.0758
.60	.5062	2.40	.2124	9.00	.0651
				10.00	.0620

TABLE VII

VALUES OF  $\bar{C}/C_0$  FOR DIFFERENT VALUES OF  $C_0/C_0'$  AND THE AUXILIARY VARIABLE  $g$  FOR A BIMOLECULAR REACTION  $C_0 \neq C_0'$  IN A LAMINARY FLOW

$g$	$C_0/C_0'$				
	0.1	0.2	0.3	0.4	0.5
0.05	0.9014	0.8911	0.8783	0.8620	0.8404
.10	.8186	.8019	.7815	.7563	.7239
.20	.6835	.6599	.6320	.5986	.5576
.30	.5770	.5507	.5203	.4850	.4431
.40	.4907	.4639	.4337	.3992	.3594
.50	.4197	.3937	.3648	.3324	.2958
.60	.3606	.3361	.3091	.2793	.2462
.70	.3110	.2882	.2635	.2364	.2068
.80	.2691	.2482	.2256	.2013	.1750
.90	.2335	.2144	.1940	.1723	.1489
1.00	.2030	.1858	.1675	.1481	.1274
1.20	.1545	.1405	.1258	.1105	.0944
1.40	.1183	.1071	.0955	.0834	.0709
1.60	.0911	.0822	.0730	.0635	.0537
1.80	.0705	.0634	.0561	.0487	.0411
2.00	.0547	.0491	.0434	.0375	.0316
2.50	.0295	.0264	.0232	.0200	.0167
3.00	.0161	.0144	.0126	.0109	.0091
3.50	.0089	.0079	.0070	.0060	.0050
4.00	.0050	.0044	.0039	.0033	.0028
4.50	.0028	.0025	.0022	.0019	.0016
5.00	.0016	.0014	.0012	.0011	.0009

$g$	$C_0/C_0'$			
	0.6	0.7	0.8	0.9
0.05	0.8104	0.7656	0.6910	0.5385
.10	.6807	.6201	.5277	.3672
.20	.5063	.4395	.3486	.2160
.30	.3927	.3304	.2513	.1467
.40	.3128	.2576	.1905	.1072
.50	.2540	.2057	.1492	.0819
.60	.2092	.1673	.1196	.0645
.70	.1742	.1380	.0975	.0519
.80	.1463	.1150	.0805	.0424
.90	.1238	.0966	.0672	.0351
1.00	.1054	.0818	.0566	.0294
1.20	.0775	.0597	.0409	.0210
1.40	.0578	.0443	.0301	.0154
1.60	.0437	.0333	.0225	.0115
1.80	.0333	.0253	.0171	.0086
2.00	.0255	.0193	.0130	.0066
2.50	.0135	.0102	.0068	.0034
3.00	.0073	.0055	.0037	.0018
3.50	.0040	.0030	.0020	.0010
4.00	.0022	.0017	.0011	.0006
4.50	.0012	.0009	.0006	.0003
5.00	.0007	.0005	.0004	.0002

and  $C_0/C_0'$ . For any initial value  $C_0/C_0'$  one determines experimentally  $\bar{C}/C_0$  as a function of  $\tau$  and then finds out the respective values of the parameter  $g$  from Table VII. Plotting  $g/(C_0' - C_0)$  versus  $\tau$  one obtains a straight line slope of which is  $(1/2)k_3$ .

In conclusion, it should be stressed that for the same residence time  $\tau$  the fraction of conversion  $\bar{C}/C_0$  is always larger for a plug flow than for a laminary flow if all the other parameters remain constant.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

## Organic Compounds in Microwave Discharge. II. Initial Studies with Toluene and Related Hydrocarbons<sup>1</sup>

BY ANDREW STREITWIESER, JR.,<sup>2</sup> AND HAROLD R. WARD<sup>3</sup>

RECEIVED OCTOBER 15, 1962

A microwave discharge of a dilute mixture of toluene in helium has been found to form principally benzene, ethylbenzene, styrene and phenylacetylene. The minor amounts of the xylenes and biaryls in the product indicate that free radicals are not important reaction intermediates. The reaction of specifically deuterated toluenes has shown that the benzene and ethylbenzene do not result from a tropylium cation intermediate. Relative reactivities and the constancy of product ratios can most reasonably result from the formation of a molecule-anion. The reactions of benzene, ethylbenzene, cycloheptatriene and bicycloheptadiene are also described. Compounds with several multiple bonds are more reactive than saturated analogs.

### Introduction

The utilization of electric discharges in chemical investigations is not recent; in their review of discharge reactions, Glocker and Lind<sup>4</sup> quote references extending back into the eighteenth century. These first investigations were sufficient to show the complexities of reactions of organic molecules in discharge, and perhaps as a result the bulk of study has been done with inorganic gases. Such discharge reactions have proved to be especially useful in the formation of free radicals from diatomic gases.<sup>5</sup>

The introduction of organic compounds to a discharge often results in the formation of a large number of products accompanied by varying amounts of tars.<sup>6</sup> Until recently, instrumental methods have been insufficient to resolve these mixtures. Schüler and co-workers have performed intensive studies on organic compounds in a high-frequency electrode discharge, most often with the view of investigating the spectra of the excited species so produced.<sup>7</sup>

Of the types of discharge available, that formed in a microwave cavity has several advantages. The discharge is formed by the high frequency field set up between the walls of cavity, and occurs in a quartz or Pyrex tube. The high frequency discharge is more efficient than one formed by direct current, since it avoids the loss of electrons by migration to an anode. It is possible to maintain a discharge at pressures of from 1 to 80 mm. so that reasonably large concentration changes are available. Most important, because the discharge is formed without electrodes, the problems common to electrode discharges are avoided. Microwave discharges have been found useful in inorganic synthesis.<sup>8</sup> In the particular case of hydrogen, 80% of the molecules can be converted into hydrogen atoms.<sup>9</sup>

Similar methods have been used in the production of nitrogen,<sup>10</sup> oxygen,<sup>10</sup> halogen<sup>11</sup> and hydroxyl radicals.<sup>12</sup> If an organic compound is placed close to (but not in) such a discharge in tritium, the rate of tritium incorporation into the molecule is greatly enhanced.<sup>13</sup>

The actual physics of the microwave discharge has received intensive study,<sup>14</sup> and the fact that atoms are produced in the effluent of a stream of molecular gas flowing through the discharge is well established, but few studies have been concerned with processes occurring directly in the discharge zone. Since electron energies can range up to about 20 e.v. in these discharges, they would seem to provide a method of study of radiation chemistry between the energies of photochemistry (up to about 6 e.v.) and radiolysis reactions (kev. to mev. range). Although intermediate energies can be obtained in a mass spectrometer, the discharge allows the investigation of neutral products and the production of materials in preparative quantities. Nevertheless, the only literature report of an organic compound reacting directly inside a microwave discharge is the conversion of methane into acetylene.<sup>15</sup> Even in this case, however, the high power level at which the discharge was maintained suggests that the reaction may have occurred in an arc rather than a glow discharge. In this paper we report some of our observations on reactions of organic compounds within a microwave glow discharge; of particular significance is our observation that certain of these reactions apparently differ from those reported in other high-energy chemistry.

### Experimental

A schematic representation of the apparatus used in the discharge reactions is shown in Fig. 1. Carrier gases (helium, USN; methane, Matheson, 99%; hydrogen, purified; all used without further purification) were fed through flow meters and needle valves, and made to flow over the organic sample. The rate of sample introduction was controlled by thermostating the sample well. Helium flow was about 0.7 l./min. at 25° and one atmosphere. Methane and hydrogen flows were 80 ml./min. under the same conditions. Toluene was thermostated at 0° for most

(1) This work has been supported in part by the National Science Foundation. A preliminary communication is treated as paper I: A. Streitwieser, Jr., and H. R. Ward, *J. Am. Chem. Soc.*, **84**, 1065 (1962).

(2) Alfred P. Sloan Fellow, 1958-1962.

(3) National Science Foundation Postdoctoral Fellow, 1961-1962.

(4) G. Glocker and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

(5) T. M. Shaw in A. M. Bass and H. P. Broida, "Formation and Trapping of Free Radicals," edited by Academic Press, Inc., New York, N. Y., 1960, p. 47; K. R. Jennings, *Quart. Rev.*, **237** (1961).

(6) The reaction of methane to give ten products and 16% tar is typical; A. W. Tickner, *Can. J. Chem.*, **39**, 87 (1961).

(7) H. Schüler and M. Stockburger, *Spectrochim. Acta*, **15**, 981 (1959); H. Schüler and E. Lutz, *Z. Naturforsch.*, **12a**, 334 (1957); H. Schüler and L. Reinebeck, *Spectrochim. Acta*, **6**, 288 (1954); H. Schüler and V. Degenhart, *Z. Naturforsch.*, **7a**, 753 (1952).

(8) W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p. 113.

(9) B. Bak and J. Rastrup-Anderson, *Acta Chem. Scand.*, **16**, 111 (1962).

(10) C. Mavroyannis and C. A. Winkler, *Can. J. Chem.*, **39**, 1601 (1961).

(11) E. A. Ogryzlo, *ibid.*, **39**, 2556 (1961).

(12) H. E. Radford, *Phys. Rev.*, **122**, 114 (1961).

(13) F. Cacace, "Proceedings of the Symposium on Chemical Effects of Nuclear Transformation," Prague, 1960, p. 133; T. W. stermark, H. Lindroth and B. Enander, *J. Appl. Rad. and Isotopes*, **7**, 331 (1960); N. A. Ghanem and T. Westermark, *J. Am. Chem. Soc.*, **82**, 4432 (1960).

(14) S. C. Brown, "Basic Data of Plasma Physics," Technology Press, Cambridge, Mass., 1959, p. 302.

(15) P. L. McCarthy, *J. Chem. Phys.*, **22**, 1360 (1954); Dr. A. P. Wolf has been studying the rearrangement of C<sup>14</sup>-labeled toluene within a microwave glow discharge as part of an extensive study of radiolysis-induced reactions (personal communication).