

The dissociation energies of a number of C_2H_3-R bonds derived from $\Delta H_f(C_2H_3) = 65 \pm 3$ kcal./mole are given in Table I. Heats of formation used are: ethylene 12.5,²⁰ propylene 4.88,²⁰ 1,3-butadiene 26.33,²⁰ vinyl chloride 8.89,²⁴ vinyl bromide 18.68²⁵ and acetylene 54.2.²⁰ The calculation of the C-H bond in vinyl radical itself reveals that the thermal stability of vinyl is probably not much greater than that of ethyl ($\bar{D}(C-H) \sim 39$ kcal./mole) or *t*-butyl ($\bar{D}(C-H) \sim 42$ kcal./mole),²⁶ assuming

(24) J. R. Lacher, E. Emery, E. Bohmfalk and J. D. Park, *J. Phys. Chem.*, **60**, 492 (1956).

(25) J. R. Lacher, A. Kianpour and J. D. Park, *ibid.*, **61**, 1125 (1957).

that the activation energies for the reverse reactions of H with the olefins and with acetylene are not greatly different.

It is interesting to note that the presently obtained values of $\Delta H_f(C_2H_3) = 65$ kcal./mole, $D(C_2H_3-H) = 105$ kcal./mole and $D(C_2H_3-Cl) = 85$ kcal./mole are almost identical with the estimates of 64, 104 and 86 kcal./mole, respectively, made some years ago by Szwarc.²⁷

(26) Based on preferred values of $D(R-H)$ given in ref. 2 and standard heats of formation of corresponding olefins.

(27) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, ISRAEL INSTITUTE OF TECHNOLOGY, AND CHEMISTRY DEPARTMENT, N. Y. STATE COLLEGE OF FORESTRY]

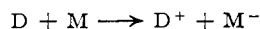
Electron-Spin Resonance Studies of Anionic Polymerization

By M. LEVY AND M. SZWARC

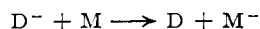
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Anionic polymerization of styrene was investigated by means of an electron-spin resonance spectrograph. No signal is shown by the solution of "living" polystyrene initiated by metallic potassium or by sodium salt of α -methylstyrene "tetramer." On the other hand, a signal, identified as that of sodium naphthalene, is shown by the solution of "living" polystyrene initiated by this reagent. Intensity of this signal was studied as a function of monomer to initiator ratio, M_{total}/I_{total} , and of temperature, and it was concluded that it arises from an incomplete consumption of initiator in the polymerization process. Furthermore, it was shown that some step of the initiation process is slow in comparison to an electron transfer process and corresponds to a higher activation energy than the propagation reaction. The nature of this step was investigated. Preliminary studies of the depropagation reaction are reported.

Two mechanisms of anionic polymerization initiation are known: the addition of a negative ion to a monomer, and the transfer of an electron from an electron donor, D or D^- , to a monomer M .^{1,2} The latter mode of initiation is represented by the equations

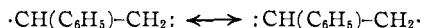


or

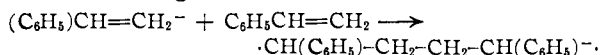


where M^- represents the primary radical-ion formed in the electron transfer process.

The primary radical-ion M^- is neither a conventional radical nor a carbanion although its structure might be represented by the two resonating forms illustrated with styrene as an example



which imply that one end of M^- acts as if it were a radical while the other acts as if it were a carbanion or *vice versa*. However, on addition of one monomer molecule to M^- a dimer is formed, possessing one "true" radical end and one "true" carbanion end, no direct interaction taking place between these two centers, *e.g.*



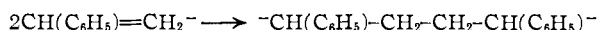
Such a dimer can result in a further polymerization of a dual character: the radical end might grow according to the rules of radical mechanism while the growth of the carbanion end would be determined by the laws of anionic polymerization. Indeed, the

(1) M. Szwarc, M. Levy and R. Milkovich, *THIS JOURNAL*, **78**, 2656 (1956).

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

work of Tobolsky and his students³ indicated that such a situation exists in copolymerization of styrene and methyl methacrylate initiated by the dispersion of metallic lithium.

Monomeric radical-ions, M^- , may also dimerize and form dimeric di-carbanions, *e.g.*



and these may continue their growth by anionic mechanism only. Whether the reaction follows this course or the one discussed in the preceding paragraph depends on the conditions of the polymerization. For example, a homogeneous initiation of styrene polymerization by sodium naphthalene is a very rapid process; it produces, therefore, a comparatively high concentration of styrene⁻ radical-ions, favoring therefore their dimerization to di-carbanions.^{1,2} On the other hand, the slow heterogeneous initiation by metallic lithium dispersion, particularly if carried out in high concentration of monomer, favors the formation of the dimeric radical-ions. The importance of the rate of initiation in determining the nature of the primary species is shown clearly by recent results of Tobolsky, *et al.*,^{3a} who repeated their experiments with styrene-methyl methacrylate mixture, initiating, however, the polymerization by sodium dispersion. Under this condition only methyl methacrylate polymerized. This can be explained by more rapid initiation by sodium as

(3) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, **31**, 123 (1958); K. F. O'Driscoll, R. J. Boudreau and A. V. Tobolsky, *ibid.*, **31**, 115 (1958).

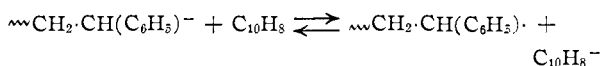
(3a) A. V. Tobolsky, D. J. Kelley, K. F. O'Driscoll and C. E. Rogers, *J. Polymer Sci.*, **28**, 425 (1958).

compared with lithium due to the lower ionization potential of the former.

Further insight into the intricacies of the electron transfer initiation requires additional investigations. With this aim in mind, the anionic polymerization of styrene has now been investigated by means of an electron-spin resonance spectrograph. Two solutions of "living" polystyrene were prepared: in one the polymerization was initiated by sodium naphthalene, while α -methylstyrene "tetramer" was employed as an initiator in the other polymerization.⁴ Hence, the first polymer results from an electron transfer reaction; the second, on the other hand, arises from an ordinary negative ion addition initiation.

It was shown that only the first solution produces a signal in the electron-spin resonance machine. Moreover, its hyperfine structure could be discerned by diluting the solution, and thus the signal was identified as that of naphthalene-radical-ion, the e.s.r. of which was reported previously by Weissman.⁵

These results demonstrate that some sodium naphthalene is left in the solution of "living" polystyrene when this reagent is used for initiating the polymerization. Its presence might be attributed either to the existence of a state of equilibrium between "living" polymers and naphthalene



or to the lack of complete consumption of sodium naphthalene in the initiation process. To clarify this point, pure naphthalene was added to the solution of "living" polystyrene initiated by α -methylstyrene "tetramer." Although the final concentration of naphthalene was as high as 0.2 M no e.s.r. absorption was observed. One concludes, therefore, that the equilibrium between "living" polystyrene and naphthalene lies too far to the left, and only an undetectable amount of naphthalene⁻ ions, if any, might be formed in such a system. The sodium naphthalene present in the solution of "living" polystyrene, when the reaction was initiated by this reagent, represents therefore its residue that was not consumed in the initiation process.

The equilibrium between "living" polystyrene and an aromatic hydrocarbon should be shifted to the right as the electron affinity of the hydrocarbon increases. To test this contention 200 mg. of anthracene⁶ was dissolved in 10 cc. of $10^{-2} M$ solution of polystyrene polymerized by metallic potassium. Although the original polystyrene solution did not show any electron-spin resonance absorption, a signal did appear on the addition of

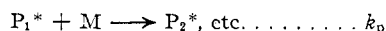
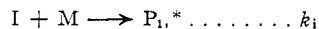
(4) α -Methylstyrene "tetramer" is prepared by treating an 0.7 M solution of α -methylstyrene in tetrahydrofuran with metallic sodium. The reaction is carried out at room temperature, and under these conditions polymerization of α -methylstyrene is thermodynamically forbidden. The product is a linear tetrameric di-carbanion which was shown to be a useful initiator of anionic polymerization. The problem of tetramerization of α -methylstyrene and of the structure of the "tetramer" will be discussed in a future publication.

(5) R. L. Ward and S. I. Weissman, *THIS JOURNAL*, **79**, 2086 (1957).

(6) The electron affinity of anthracene is considerably higher than that of naphthalene.

anthracene, and was identified as that of anthracene⁻ radical-ion. The presence of this radical-ion also could be inferred from the optical spectrum of the solution, which showed a peak at 725 $m\mu$ characteristic of anthracene mono-negative radical-ions.

We shall proceed now to show that the consumption of the initiator in a polymerization process not involving termination must always be incomplete. This is a consequence of the fact that the growing chains compete for the monomer with the initiator. To make clear this point, let us consider a polymerization the kinetics of which is determined by the equations



Solution of the appropriate differential equations gives f , the fraction of the utilized initiator, as an implicit function of k_p/k_i and $M_{\text{total}}/I_{\text{total}}$, the last two symbols denoting the total amount of monomer and initiator introduced into the reacting system.^{6a}

$$M_{\text{total}}/I_{\text{total}} = (k_p/k_i) \cdot \{\ln(1-f)^{-1} - f\} + f$$

Values of f computed for selected values of k_p/k_i and $M_{\text{total}}/I_{\text{total}}$ are listed in Table I. Inspection of this table shows that f decreases with decreasing ratio of $M_{\text{total}}/I_{\text{total}}$ or increasing ratio of k_p/k_i . These theoretical calculations were verified qualitatively by the following experiments: 0.26 mmole of styrene was polymerized at room temperature with 0.23 mmole of sodium naphthalene dissolved in 5.7 cc. of tetrahydrofuran. The electron-spin resonance absorption showed presence of approximately 25% of the original sodium naphthalene in the solution. On the other hand, when a 100-fold excess of styrene was used, only 1% of the original electron-spin resonance absorption was shown by the resulting solution.

TABLE I

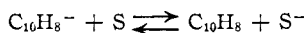
k_p/k_i	$M_{\text{total}}/I_{\text{total}}$	f
0.1	5	> 0.99
0.5	5	> .99
1.0	5	.99
2.0	5	.97
2.0	8	.99
5.0	5	.81
5.0	7	.90
5.0	20	.99
10	5	.67
10	10	.82
10	20	.95
100	10	.38
100	50	.69
100	100	.84

The last experiment was repeated at -78° , and the electron-spin resonance absorption, determined after completion of the polymerization, showed now 8% of the original absorption, exhibiting the hyperfine structure of sodium naphthalene. One concludes, therefore, that the activation energy of the over-all initiation process is

(6a) One should notice that the rate of addition of monomer to the initiator solution is not affecting at all the value of f , as long as the above-suggested kinetic scheme applies.

greater than the activation energy of the propagation process.⁷

We should consider more thoroughly the electron transfer initiation and concentrate our attention on the reaction involving sodium naphthalene. The electron transfer from naphthalene⁻ radical-ion to styrene molecule must be the first step of the initiation, and the work of Weissman⁵ suggests that this reaction is very rapid, corresponding to a bimolecular rate constant of the order 10^7 – 10^9 in units $\text{l. mole}^{-1} \text{ sec.}^{-1}$. Hence, the electron transfer process should lead rapidly to the equilibrium



This equilibrium is different from the earlier discussed equilibrium involving naphthalene⁻ radical-ions and "living" polystyrene, since the monomeric styrene⁻ radical-ion (S^-) is an entirely different species than polystyrene carbanion. The equilibrium constant of this process may be estimated approximately from the first reduction half wave potential.^{8,9} Using the values published for naphthalene and styrene we calculate that at equilibrium the concentration of the coexisting ions (N^- and S^-) should be comparable if a mixture contains only a small excess of styrene. The same type of calculations indicates that the equilibrium greatly favors S^- ions if sodium biphenyl is used as an initiator, while the anthracene⁻ radical-ions are favored in a reaction of monosodium anthracene with styrene.¹⁰ In conformity with these calculations it is observed that no electron-spin resonance absorption is shown when styrene is polymerized by sodium biphenyl ($M_{\text{total}}/I_{\text{total}} = 3/2$), only for $M_{\text{total}}/I_{\text{total}}$ slightly greater than unity a signal, having the hyperfine structure of biphenyl⁻ radical-ion, is detectable. On the other hand, sodium anthracene was indeed shown to be a poor initiator of anionic polymerization of styrene.

The facts presented in this paper lead to two conclusions: first, some step in the initiation process is relatively slow, particularly at low temperatures, and corresponds to a higher activation energy than the propagation reaction; and second, no electron-spin resonance absorption of S^- radical-ion can be detected in the system. It is unlikely, as was pointed out earlier, that the electron transfer process is so slow, and hence one concludes that it is the dimerization of S^- radical-ions and the addition of the first molecule of monomer to S^- which must be the relatively slow reactions. Slowness of reactions involving S^- radical-ions is not surprising. The recombination of S^- radical-ions is hindered by coulombic repulsion, and since

(7) It might be desirable to give here some numerical data for the pertinent rate constants. Rate constant of propagation, k_p , is certainly not greater than $10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. For this k_p over 99% of polymerization will take place in 1 sec. under conditions of our experiments. From the values reported here we calculate k_p/k_i to be in the range of 0.4–30 at room temperature, and still greater at -78° . Hence, k_i is expected to be of the order of 10^4 or less, while the rate constant for electron transfer process is of the order of 10^7 – 10^9 in the same units.

(8) G. J. Hoijtink, *Rec. trav. chim. (Pays-Bas)*, **74**, 1525 (1955); **76**, 869 (1957); G. J. Hoijtink, *et al.*, *ibid.*, **75**, 487 (1956).

(9) H. A. Laitinen and S. Wawzonek, *THIS JOURNAL*, **64**, 1765 (1942).

(10) The 1st reduction half-wave potentials are 2.80 v. for biphenyl, 2.50 v. for naphthalene, 2.37 v. for styrene, and 1.98 v. for anthracene. These values refer to 96% dioxane–water solution.

these species are not conventional free radicals their reactivity in the dimerization might be substantially lower than that of free radicals. Moreover, the S^- radical-ions are not genuine carbanions either; hence their reactivity toward the monomer is also expected to be lower than that of carbanion ends of "living" polymers.

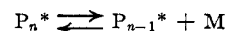
It is difficult to decide which of these two relatively slow reactions is the faster one. The dimerization reaction is second order in respect to S^- , while the addition of the first monomeric molecule is first order in S^- but it depends on monomer concentration. It is probable that during the first period of the initiation process dimerization is faster, but in the later stages of the reaction the addition of the monomer might overtake the dimerization.

There is an apparent contradiction in assuming a rapid electron transfer process followed by a relatively slow reaction of S^- radical-ions. If the electron transfer reaction is rapid, and the disappearance of S^- , say by its dimerization, is slow, then the S^- radical-ions should be left at the end of polymerization. Examination of the hyperfine structure of the electron-spin resonance signal showed, however, that it was sodium naphthalene which was left in the reaction. This apparent contradiction is resolved easily if one recalls that the reaction



is also very rapid and that the monomer, S, is consumed continuously by the propagation reaction. Hence, even if the concentration of S^- radical-ions were high during the last stages of polymerization, its reaction with naphthalene would regenerate styrene and the removal of the latter by the propagation step would shift the reaction further and further toward formation of $\text{S} + \text{N}^-$. Thus, indeed, it should be N^- and not S^- that is left unreacted at the completion of the polymerization.

The interaction between styrene, naphthalene and their respective negative ions has an interesting ramification. Since the polymerization yields "living" polymers, and these exist in equilibrium with the monomer,^{11–13} the concentration of the monomer must remain constant, equal to the equilibrium constant of the reaction



as long as "living" polymers are present in the solution. Hence, if a solution of sodium naphthalene is added, say, to a solution of "living" polystyrene, sodium naphthalene should disappear slowly as a result of its reaction with the residual monomer. This reaction is much slower than the initiation of the polymerization on account of the extremely low concentration of styrene (the equilibrium concentration of styrene is estimated to be $10^{-7} M$ at room temperature).

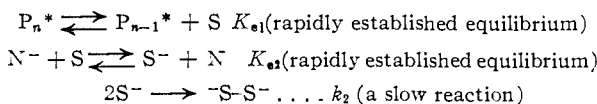
Preliminary experiments confirm fully these conclusions. Although a solution of sodium naphthalene is stable in absence of "living" polymers, the color slowly fades in their presence. The rate of

(11) H. W. McCormick, *J. Polymer Sci.*, **25**, 488 (1957).

(12) D. J. Worsfold and S. Bywater, *ibid.*, **26**, 299 (1957).

(13) W. B. Brown and M. Szwarc, *Trans. Faraday Soc.*, **54**, 416 (1958).

disappearance of N^- was shown to be second order in respect to N^- and an addition of naphthalene causes a decrease in the rate. The following mechanism is proposed to account for these observations



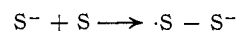
This scheme leads to the expression

$$-dN^-/dt = k_2(K_{e1}K_{e2})^2 \times (N^-/N)^2,$$

agreeing well with the experimental findings. Furthermore, when sodium biphenyl was added instead of sodium naphthalene, the rate of disappearance of biphenyl $^-$ radical-ion was found to be greater than that of naphthalene $^-$ radical ion. This is accounted for by the proposed mechanism since K_{e2} is greater for biphenyl than for naphtha-

lene. Further studies of the depropagation of "living" polymers are being continued.

The last series of experiments, preliminarily reported here, confirms the relative slowness of the dimerization of S^- radical-ions. Of course, the conditions of these experiments were such that the addition reaction



must be even slower, because of the exceedingly low concentration of the monomer. This is certainly not the case in the initial stages of the polymerization.

In conclusion, we wish to thank the National Science Foundation for financial support of these investigations through the grant No. G-2761.

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[CONTRIBUTION FROM THE BROOKHAVEN NATIONAL LABORATORY, AND THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The D_2O - H_2O Solvent Effect on a Complex Ion Equilibrium*

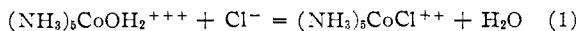
BY HENRY TAUBE

RECEIVED JULY 24, 1959

The change in solvent from H_2O to D_2O increases the equilibrium quotient for the reaction $(NH_3)_5CoOH_2^{+++} + Cl^- = (NH_3)_5CoCl^{++} + H_2O$ by the factor 1.5. Comparisons of the effect observed here with that of the corresponding reaction, but with OH^- replacing Cl^- , are made.

The study of the influence of the change in solvent from H_2O to D_2O on the rate of electron transfer^{1,2} has directed attention to the effect of this solvent change on some equilibria which are relevant to the problem of electron transfer. Thus it has been shown that K_{diss} for Fe^{+++} aq. is unchanged¹ by substituting D_2O for H_2O , and that K_{diss} for $(NH_3)_5CoOH_2^{+++}$ is decreased by a factor of 1.5 when this change is made in the isotopic composition of the solvent.³ The hydrogen-isotopic solvent effects for these aquo ions are considerably smaller than those reported⁴ for oxyacids having the same values of K_{diss} . In the context of these observations and considerations, it seemed of interest to measure the magnitude of the effect which the H_2O - D_2O solvent change has on a complex ion equilibrium which does not involve a proton-containing ligand as the group being replaced by H_2O . By comparing the results for such a system with those obtained for the corresponding one in which OH^- is replaced by H_2O , we can hope to assess the contribution to the isotope effect made by the OH bond in OH^- .

The reaction



was chosen for study. Because the rates of substitution are slow, but not too slow, the system is tractable and the equilibrium quotients can

be measured readily by spectrophotometric means. The system has the added virtue that a complete description of the reaction is possible, at least insofar as the first sphere of coordination is concerned; for a substitution-labile system an equally complete description of the reaction is not always possible.

Experimental

$(NH_3)_5CoOH_2(ClO_4)_3$ prepared as described earlier⁵ and purified by repeated crystallization was the source of the ion $(NH_3)_5CoOH_2^{+++}$, and the salt $(ND_3)_5CoCl_3$, similarly purified, was the source of the chloro-complex. The extinction coefficients of the deuterio forms of the complex ions are sufficiently different⁶ from those of the ordinary forms so that it was necessary to determine them also. The deuterio form of the aquo ion was prepared simply by dissolving $(NH_3)_5CoOH_2(ClO_4)_3$ in the deuterated solvent and waiting for exchange equilibrium. $(NH_3)_5CoCl_3$ was prepared by the method described by Adamson and Basolo.⁶

The equilibrium quotients were determined by measuring the optical densities of the limiting forms $((NH_3)_5CoOH_2^{+++}$ and $(NH_3)_5CoCl^{++}$), having the isotopic composition of the ions the same as that of the media, and comparing these optical densities with those measured for solutions which had reached equilibrium. At 25° a period of one month was allowed for equilibration, but at 51° a period of 2 days suffices, and at the highest temperature 80° a period of 3 hours. Solutions equilibrated at the higher temperatures were cooled rapidly to freeze the equilibrium. Measurements of optical density always were made at room temperature so that no corrections for the change in extinction coefficients with temperature were needed. The optical densities reported were measured with a Cary spectrophotometer, Model 14, the range from 650 to 310 μ being covered.

The deuterium enriched solutions contained 87% D_2O . All solutions were made 0.003 M in $HClO_4$ (acid is added to

* Research performed under the auspices of the U. S. Atomic Energy Commission.

(1) J. Hudis and R. W. Dodson, *THIS JOURNAL*, **78**, 911 (1956).

(2) A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

(3) D. J. Bearcroft, D. Sebera, A. Zwickel and H. Taube, to be published.

(4) G. Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

(5) A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 835 (1952)

(6) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).