other, bonding between the carbonyl oxygen with either the Li ion or the water of the Li hydration shell has been postulated.[41] It should therefore be expected that a similar type of complexing will occur with the peptide group along a polymer chain. Clarification of the details of the binding will allow an understanding of the resulting bond structure. The possibility of the formation of cyclic structures between successive pairs of amino acid residues resulting from Li ion binding can also be given consideration.

Thus, a basis exists for the expectation of structural alteration of the repeating units as a result of interactions with aqueous LiBr solutions. When present in sufficient concentration, the newly formed structure could crystallize in a new type lattice. In this connection it is important to note that polyglycine can exist in a crystallographic structure, where X-ray diffraction and infrared studies show that the conformation of the polypeptide chain differs significantly from either that of the α-helix or the normal β forms.[52] Pertinent to the present study is the fact that one of the ways in which this form of polyglycine is prepared is by precipitation of the polymer with water from an aqueous LiBr solution, polyglycine being normally insoluble in pure water. For the case of α-keratin immersed in LiBr solutions, Hambraeus and Steele[17] claim that at room temperature for solutions of 5M concentration and above, a new X-ray diagram of the fiber was obtained. We have not, however, been able to unequivocally substantiate the latter report. Thus, some evidence exists, as yet inconclusive, which supports the concept of the formation of a new crystallographic structure and which is consistent with the postulated mechanism of chemical melting.

It is clear, however, that a quantitative understanding of the chemical processes involved in the melting is incomplete. Despite this shortcoming, it has been demonstrated that the crystal–liquid transformation in the fibrous proteins can be controlled by chemical reactions. The distinction made between the contractile process and the reactions which induce melting thus appear to be justified. Contractility in the fibrous proteins by this general mechanism, resulting from interaction with other species, therefore can be expected.

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(52) C. H. Bamford, L. Brown, E. M. Cant, A. Elliot, W. E. Hanky and B. R. Malcolm, *Nature*, **176**, 396 (1955).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Initiation of Methyl Methacrylate by Aromatic Radical-anions

BY ARTHUR V. TOBOLSKY AND DAVID B. HARTLEY

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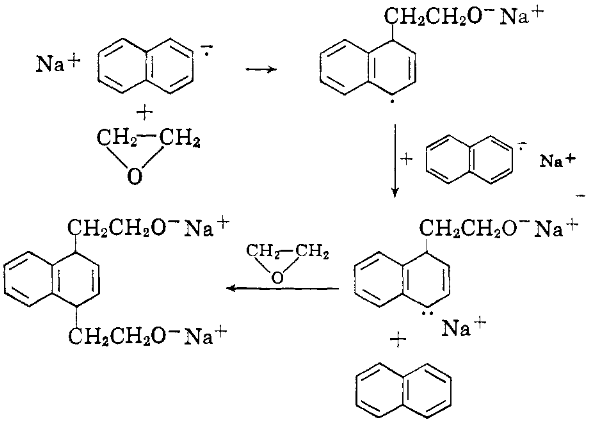
Methyl methacrylate has been polymerized by a variety of aromatic hydrocarbon radical-ions. Some initiators were found to induce polymerization by electron transfer, others by bond formation with the methacrylate. The mechanism of initiation appears to be governed to a large extent by the orbital energy of the initiator and to be more or less independent of the counterion.

Introduction

The importance of radical-ions as initiators of anionic polymerization has been recognized since the realization by Szwarc[1,2] that the initiation of styrene by sodium naphthalene proceeds by an electron transfer mechanism regenerating free naphthalene. Sodium naphthalene also initiates α-methyl styrene by electron transfer and these monomers have also been polymerized by other radical-anions.

It has recently been demonstrated by Tobolsky, Rembaum and Eisenberg[3] that in the polymerization of α-methyl styrene by monosodium diphenyl acetylene a bond is formed between the initiating molecule and the polymer. The mechanism of initiation in this particular case is obviously quite different from a mere electron transfer.

Bond formation in the initiation of other monomers by radical-ions is not unknown—this is the manner in which sodium naphthalene for example opens siloxane rings.[4] Equally striking is the mechanism by means of which the same complex initiates polymerization in ethylene oxide.[4,5] The reaction schemes for these two cases are similar and are represented by



and the 1,2- addition product.

These examples together are sufficient indication that the mode of initiation by a radical-ion depends on both initiator and monomer. It cannot

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

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

(3) A. V. Tobolsky, A. Rembaum and A. Eisenberg, *J. Polymer Sci.*, **45**, 347 (1960).

(4) M. Morton, A. Rembaum and E. E. Bostick, *ibid.*, **32**, 530 (1958).

(5) D. H. Richards and M. Szwarc, *Trans. Faraday Soc.*, **55**, 1644 (1959).

be said that because a given initiator reacts by one mechanism with a particular monomer it will behave in the same way towards other monomers; nor will other radical-ions necessarily initiate a particular monomer all by the same mechanism.

The present paper examines a number of alkali metal aromatic hydrocarbon complexes with respect to their mechanism of initiation of methyl methacrylate. It will be shown that some initiate *via* electron transfer, others initiate *via* bond formation, and a rationale for these differences is discussed.

Experimental

Purification of Materials.—The solvent employed was Mathieson tetrahydrofuran. This was purified by refluxing for three or four days over sodium–potassium alloy, distilling from the sludge produced and further refluxing for half a day over fresh alloy. Addition of a small quantity of naphthalene at this stage produced the alkali metal complex, and the green solution was then degassed on the vacuum line.

Methyl methacrylate, containing 0.006% hydroquinone, was obtained from Borden Chemical Company. It was washed twice with 5% caustic soda to remove the inhibitor and twice with water. After drying for a few hours over calcium chloride and then over calcium hydride, it was distilled from the latter under reduced pressure. The distillate was treated with calcium hydride under vacuum for two days until degassing was complete. Thereafter it was maintained in liquid nitrogen. When required for use approximately 2 cc. of monomer was distilled into well-flamed, weighed ampoules and its weight determined. Samples were kept at about 5° and were never allowed to age more than a week before being used.

Aromatic hydrocarbons, for the preparation of initiators, were of good reagent grade and used as supplied by the manufacturers (Aldrich Chemical Company); except in the case of acenaphthylene which was sublimed under vacuum before use.

Preparation of Initiators.—On account of the apparent tendency of some radical-ions to decompose on prolonged standing, initiator solutions were prepared singly and used immediately. The preparative techniques used were minor modifications of those presented earlier.[3]

Polymerization.—To carry out a polymerization, initiator and monomer ampoules were blown on to two arms of a three-necked flask, each equipped with a magnetic breaker. A constriction and joint on the third arm permitted thorough evacuation. An appropriate amount of solvent to make the total volume about 30 cc. was distilled into the flask, which was then removed from the vacuum line.

The initiator was first introduced into the bulb (in the case of Li^+ $Hydrocarbon^-$ initiators the lithium stick remained in the ampoule), followed by the methyl methacrylate, and polymerization was allowed to proceed.

It was found that particularly with a sodium counterion, and apparently independently of the associated generator, decomposition of the original polymer took place if polymerization was continued beyond a couple of hours or so, the decomposition product tending to mask any ultraviolet absorption due to formation of a bond between initiator and polymer.

In general then the polymer was terminated after an hour or two, by addition of methanol. The polymer was precipitated at least three times, from benzene, chloroform or t.h.f. as seemed most suitable for removing initiator traces, by pouring into methanol. The filtered polymer was dried in a vacuum oven for 12–16 hr. or so at 40°

Analysis.—Analysis of the polymer for aromatic residues bonded to the methyl methacrylate in the initiation step was accomplished by determining its ultraviolet absorption spectrum in chloroform, using a Warren Spectracord, or for more quantitative determinations a Cary Spectrophotometer. Pure poly methylmethacrylate has no absorption between 360 and 250 mμ (the range of the spectral measurements) and was chosen for the present study because it allows easy detection of aromatic groups.

In order to confirm that the washing of a polymer was adequate and all traces of free generator had been removed, inspection of the visible absorption often proved useful. In cases which still remained in doubt the original quantitative ultraviolet and visible spectral determinations were followed by further precipitations until a constant spectrum was obtained.

When bond formation occurred this was expected to produce a dihydro type of derivative of the generator in the polymer (compare refs. 4,5,6). In these cases the observed spectra were found to agree well with the spectra of the dihydro compounds where the latter were known, *e.g.* 9,10-dihydroanthracene. In instances where no comparison with dihydro spectra was available, and where the generator molecules absorbed in the visible as well as ultraviolet, washed polymer absorbing in the ultraviolet but not in the visible was indication that a bond had formed. If the presence of an aromatic residue showed up in a spectrum, this was invariably found to differ considerably from the spectrum of the pure generator.

Results and Discussion

The results obtained by interpreting the polymer spectra on the above bases are summarized in Table I. Also included in Table I is the so-called Hückel "orbital energy" of each generator. This is the lowest unfilled molecular energy level of the hydrocarbon, into which the extra electron in the anion will go.

TABLE I

	Mechanism		
Generator	Li counterion	Na counterion	Orbital energy in units of $-\beta$
Biphenyl	Transfer	Transfer	0.705
Naphthalene	Transfer	Transfer	.618
Phenanthrene	Bonding	Bonding	.605
Stilbene	Transfer	Transfer	.504
Diphenylacetylene	Bonding	Bonding	.504
Anthracene	Bonding	Bonding	.414
Diphenylbutadiene	Bonding	Bonding	.386
Tetraphenylethylene	Transfer	.....[a]	.368
Perylene	.....[b]	Bonding	.347
Naphthacene	Bonding	Bonding	.295
Acenaphthylene	Bonding	Bonding	.285

[a] Monosodium complex unobtainable. The red disodium compound forms immediately. With lithium a strong purple color preceded the formation of the red, and this was assumed to be a mono complex. [b] Low solubility of hydrocarbon, combined with slow rate of formation of the lithium salt, made study of this initiator impracticable.

A low-lying orbital energy level implies a high electron affinity and, as might therefore be expected, a reduced tendency for the anion to undergo electron transfer. It is indeed apparent from the tabulated results that with the exceptions of phenanthrene and tetraphenyl ethylene, it is the anions of hydrocarbons with a high orbital energy which initiate methyl methacrylate by electron transfer.

Electron affinity is not, however, the complete explanation of why some initiators react with a given monomer in one way while others react by the alternative mechanism, though it seems to be an important factor. For it is conceivable that an initiator with a high tendency to lose an electron might have an even greater inclination to form a bond, in which case the latter mechanism would operate. Similarly a high electron affinity is no definite indication that bond formation is to be preferred: electron transfer may take place by default of the bonding reaction. In these terms we could possibly interpret the "anomalies" of phen-

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(6) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

anthrene and tetraphenyl ethylene, through the behaviour of the latter could also be ascribed to a steric effect.

There is good reason to believe that the mechanism is also dependent on the vinyl monomer being initiated. This dependence was not shown up in the present study which was restricted to the polymerization of methyl methacrylate.

A further point of interest in the experimental results lies in the observation that mechanism appears to be more or less independent of cation. Presumably the environmental differences brought about by changing the alkali metal have an insignificant effect on the energetic factors which determine the mechanism.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., CANADA]

The Thermal Decomposition of Octafluorocyclobutane[1]

BY JAMES N. BUTLER

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Octafluorocyclobutane undergoes a reversible first-order thermal decomposition to tetrafluoroethylene in the temperature range from 360 to 560° with rate constant $k_1 = 10^{16.0}\ e^{-74,300\ \text{cal.}/RT}$ sec.$^{-1}$ and equilibrium constant $K_c = 10^{8.6}\ e^{-49,900\ \text{cal.}/RT}$ mole/l. A parallel decomposition forming hexafluoropropene occurs with first-order rate constant $K_3 = 10^{17.2}\ e^{-87,000\ \text{cal.}/RT}$ sec.$^{-1}$. The pressure dependence of k_1 and the decrease of activation energy at low pressures can be described by the classical theory of unimolecular reactions with approximately 20 of the 30 possible normal modes of vibration participating in the reaction. At pressures below 0.05 mm. the rate becomes pressure-independent, due to a slow heterogeneous reaction with the same activation energy as the homogeneous reaction. The rate of formation of C_3F_6 is primarily homogeneous under the conditions used. The rate of formation of C_2F_4 is enhanced by traces of oxygen, but the rate of formation of C_3F_6 is unaffected. No satisfactory results were obtained with inert gases, probably due to traces of oxygen. Side reactions with the walls of the pyrex vessel producing CO, CO_2, SiF_4, and possibly COF_2 were observed and corrected for in the calculations.

Introduction

The thermal decomposition of octafluorocyclobutane was briefly studied by Atkinson and coworkers in the course of their work on the thermal decomposition of tetrafluoroethylene.[2,3] At temperatures below 550°, the only fluorocarbons formed from octafluorocyclobutane are tetrafluoroethylene and hexafluoropropene. Gray and Pritchard[4] attempted to measure the rate of decomposition of octafluorocyclobutane by following the rise in pressure but found that the fluorocarbons attacked Pyrex producing silicon tetrafluoride and carbon monoxide. As a result, no useful data could be obtained by this method except at pressures of 300 mm. or greater.

The present work was undertaken to find out if the decomposition of octafluorocyclobutane was described by the theory of unimolecular reactions in spite of the complications occurring. Using gas chromatography for analysis, the rate of reaction can be followed by measuring the ratios of products after a definite length of time even though side reactions may occur. This method also allows the reaction to be studied at much lower temperatures and pressures than was heretofore possible.

Experimental

Furnace. Experiments were carried out in a one-liter spherical Pyrex flask kept at constant temperature by an electrically heated air bath. The temperature was controlled by operating the furnace from a variac and voltage regulating transformer and enclosing the furnace in an insulated copper drum which was cooled by circulating tap water at 8° through coils fastened to its outside. When a steady state had been established at 500°, the temperature of the flask varied less than 0.5° over a period of an hour. Temperature measurements were made using three chromel–alumel thermocouples. The one on the bottom of the flask consistently read about five degrees lower than the two at mid height, one of which read about half a degree higher than the other. The temperature of the gas in the flask was taken to be the average of the three readings. It is estimated that the absolute value of the temperature measurements may be in error by one or two degrees but that the relative values are consistent to less than 0.5 degrees. A 100 ml. reactor packed with glass wool was also used. Pressure measurements were made with a wide-bore manometer or McLeod gauge. The tubing connecting the 1-liter reactor to the vacuum system was 10 mm. or larger to minimize thermal transpiration effects.

Materials.—A sample of octafluorocyclobutane was donated by the Research Division of E. I. du Pont de Nemours and Co., Wilmington, Delaware. It was analyzed by gas chromatography, the only impurity being 0.005% tetrafluoroethylene. Tetrafluoroethylene and hexafluoropropene were prepared by pyrolysis of Teflon scraps in a quartz tube at a temperature of approximately 600° and a pressure of approximately 10^{-2} mm. The gas evolved was collected in a trap cooled with liquid nitrogen and consisted of 95% C_2F_4, 4% C_3F_6 and 1% C_4F_8, with traces of higher fluorocarbons. The components were separated and purified by gas chromatography on a two-meter silica gel column. The purified tetrafluoroethylene contained 0.1% C_3F_6 and less than 0.005% C_4F_8. It was stored as a gas at about 50 mm. pressure and showed no signs of polymerization or decomposition in a period of a year. Tetrafluoromethane, used as an inert gas, also was donated by the duPont Co. It contained 0.05% C_3F_8 and less than 0.1% C_2F_6. Prepurified nitrogen and Research Grade argon obtained from the Matheson Company also were used as inert gases.

Sampling and Analysis.—At the end of a run, the gas in the reactor was expanded into a dead space of about 20 ml. volume, this gas being discarded. The remainder of the gas was expanded into a one-liter bulb at room temperature. This bulb was detached and taken to the gas chromatograph. A Toepler pump was used to transfer the gas from the sample bulb to the 15 ml. sample loop through which the

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(1) Presented at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, 6-12 August, 1961.

(2) B. Atkinson and A. B. Trenwith, *J. Chem. Soc. (London)*, 2082 (1953).

(3) B. Atkinson and V. A. Atkinson, *ibid.*, 2086 (1957).

(4) B. F. Gray and H. O. Pritchard, *ibid.*, 1002 (1956).