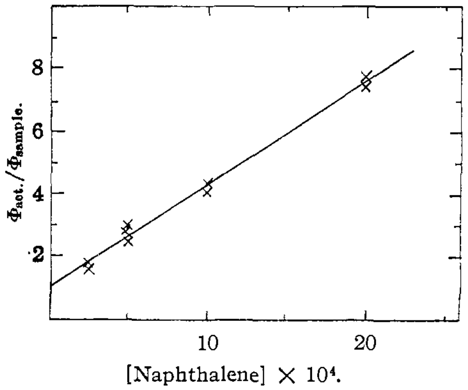

Fig. 2.—Photoreduction of 0.1 *M* benzophenone with naphthalene and 0.10 *M* benzhydrol in benzene solution (actinometer solution contained 0.10 *M* benzhydrol, no naphthalene), slope 3350., intercept 1.0.

also be diffusion controlled even though quenching occurs by a different energy dissipation mechanism. Oxygen and other paramagnetic substances are postulated to quench triplet states through the perturbation caused by the uncoupled spins. Evans,[10] in his study of singlet to triplet absorption spectra which are produced under the influence of high oxygen pressures, has vividly demonstrated paramagnetic perturbation on electronic transitions.

Molecules such as naphthalene, which are diamagnetic, must quench triplet states because of the favorable position of their lowest triplet state. Recently, two communications[11] have shown the practical application of predicted photosensitization with acceptors possessing triplet states of lower energy levels than benzophenone.

From the ratio k_q/k_r, it would appear that naphthalene is more efficient as a quencher than oxygen. This may be due to the fact that oxygen slowly reacts with the benzophenone–benzhydrol system while naphthalene is chemically inert.[1]

Acknowledgments.—This work was supported by a grant from the Utah State University Research Council. One of us (M. K.) is grateful to the National Science Foundation for an undergraduate summer research fellowship.

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[10] D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

[11] G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2395, 2396 (1961).

CONTRIBUTION FROM NOYES CHEMICAL LABORATORY UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

The Infrared and Nuclear Magnetic Resonance Spectra of Ethyllithium

BY THEODORE L. BROWN, D. W. DICKERHOOF[1] AND D. A. BAFUS

RECEIVED OCTOBER 4, 1961

The infrared spectra for ethyllithium in hydrocarbon solvents, in a Nujol mull, and as a solidified melt are reported. Some bands previously associated with various associated and non-associated species of ethyllithium are shown to be due to lithium ethoxide. The proton and lithium n.m.r. spectra are reported. The spectral results, along with other experimental observations, suggest that ethyllithium exists as a single species in hydrocarbon solvent, probably as a hexamer. Models for both a hexamer and tetramer form of ethyllithium are presented and discussed in terms of the presently known properties of the compound.

Introduction

The structures and physical properties of lithium alkyls have been of considerable interest for many years. Recent infrared[2] and mass spectral[3] studies have shed new light on the properties of ethyllithium in both solution and the vapor phase.

It has become clear in the course of our work with lithium alkyls that decomposition has been an important factor in earlier incorrect interpretations of infrared spectral and other experimental results. In the work reported here we have identified the decomposition products which give rise to spurious absorptions in the spectra and have obtained data for material free from decomposition. Infrared and n.m.r. spectra for ethyllithium in hydrocarbon solvents are reported. Models for the structures of the compound in solution and in the vapor phase are proposed and discussed.

Experimental

Materials.—Lithium.—Lithium metal was obtained from Lithium Corp. of America or Maywood Chemical Works. Both bulk form or dispersions (the latter obtained from Lithium Corp. of America) were employed.

Ethyllithium.—Ethyllithium was prepared by methods previously described.[4] All results reported were obtained with samples which were recrystallized from an appropriate solvent (pentane, hexane, cyclohexane or benzene) in an inert atmosphere box.[5]

Solvents.—Reagent grade benzene was dried over sodium wire before use. Commercial grade cyclohexane, hexane and pentane were chromatographed through acid-washed alumina and stored over sodium wire. All solvents were thoroughly deaerated by flushing with argon before they were placed in the inert atmosphere box.

Lithium Ethoxide.—200 ml. of dry benzene was placed in a 500 ml. round-bottom flask under dry nitrogen. To this were added 3.5 g. (0.5 mole) of lithium metal and 29.2 ml. (0.5 mole) of absolute ethanol. The reaction was allowed to proceed to completion and benzene then removed by distillation at reduced pressure. Lithium ethoxide remains as a white amorphous solid.

Variations in the above procedure were also carried out. In one preparation a 50% excess of ethanol was employed. After removal of the solvent the white solid was heated for a time to remove the last trace of ethanol. On another occasion less than the stoichiometric quantity of ethanol was employed. The lithium ethoxide prepared in this instance was contaminated with lithium metal, but there was presumably no unreacted alcohol present.

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[1] Department of Chemistry, Colorado School of Mines, Golden, Colorado.

[2] R. West and W. H. Glaze, *J. Am. Chem. Soc.*, **83**, 3580 (1961).

[3] J. Berkowitz, D. A. Bafus and T. L. Brown, *J. Phys. Chem.*, **65**, 1380 (1961).

[4] T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).

[5] The design of the purge system employed with the box will be described in *Rev. Sci. Instr.*, 1962.

Attempts to further purify lithium ethoxide were not successful. It does not sublime nor is it appreciably soluble in solvents other than alcohol. The materials produced in all of the preparations showed essentially identical spectra. The only obvious evidence of impurity was a very weak absorption in the 3600 cm.$^{-1}$ region, presumably due to lithium hydroxide. Before use the ethoxide was washed thoroughly with benzene or cyclohexane, after which the solvent was removed by filtration.

Solutions.—Solutions were made up in an inert atmosphere box. For some of the work it was necessary to determine the concentration of ethyllithium by chemical means. Aliquots of the solutions were decomposed with water, an excess of standard acid solution added, and the solution back-titrated with standard base solution using phenolphthalein as indicator.

Infrared Spectra.—Infrared spectra were obtained using a Beckman IR-7 spectrophotometer in the range 650–4000 cm.$^{-1}$. Solution spectra were obtained for the most part in cells with sodium chloride windows and path lengths of about 0.4 mm. All cell thicknesses were determined by the interference fringe method. The instrument was operated in double-beam operation, and solvent background traces were obtained for each solution spectrum from which quantitative results were desired.

N.m.r. Spectra.—Samples of ethyllithium solutions in benzene were sealed in 5 mm. Pyrex tubes; spectra were obtained using a Varian Associates 4300 B spectrometer. No internal standard was added to the solutions in the proton resonance work. Aqueous lithium bromide solutions, 70% and 7% hydrated lithium bromide by weight, were employed as external references in the lithium resonance spectra. The proton resonance spectra were obtained using a 60 mc. probe, the lithium resonance spectra with a 15.1 mc. probe at a field of about 9130 gauss.

Results

Infrared Spectra.—A number of bands present in previously reported spectra of ethyllithium[2,4,6,7] are due to lithium ethoxide. The mull spectrum of the ethoxide, Table I, corresponds closely to a number of the bands present in many "ethyllithium" spectra.[8] These bands are either completely absent or of very low intensity in the solution spectra of carefully purified ethyllithium. Furthermore, the solution which results from placing a pure ethyllithium solution in contact with solid lithium ethoxide gives precisely the same spectrum as a solution which has been exposed to an oxygen-containing atmosphere. By adding the appropriate quantity of the ethoxide, it was found possible to duplicate many of the previously reported spectra.

TABLE I

INFRARED SPECTRUM OF LITHIUM ETHOXIDE

Values in parentheses were obtained from perfluorokerosene mull, the others from a Nujol mull.

844 (s)	(2605) (w)
1063 (s)	(2715) (m)
1116 (s)	(2805) (s)
1156 (vw)	(2907) (s)
1384 (s)	(2953) (s)
1461 (s)	

It is of some interest that although lithium ethoxide is very readily soluble in benzene solutions of ethyllithium, it is not appreciably soluble in benzene itself. This suggests that a complex is formed between ethoxide and lithium alkyl (see later).

Spectra of ethyllithium in benzene are shown in Fig. 1. The regions of strong benzene absorption are shown by the lines near the bottom of the figure. The absorbance of the 923 cm.$^{-1}$ band follows Beer's law over a wide range of concentration, 0.03–1.2 *M*. An estimate of the integrated intensity using Ramsay's formula[9] yields a value of 0.85×10^4 mole^{-1} l. cm.$^{-2}$. The spectra of ethyllithium in hexane and cyclohexane are, in their general features, the same as those in benzene solution. Spectra of both benzene and hexane solutions were examined at temperatures of 30.0, 40.0 and 50.0°. Aside from a slight broadening of the 923 cm.$^{-1}$ band with an increase in temperature, no changes in the spectra in the 850–1300 cm.$^{-1}$ region were observed. Shigorin, on the other hand, reports quite marked changes in spectra with change in temperature.[6c] The bands which he reports as increasing in intensity with increasing temperature (at 1050 and 1100 cm.$^{-1}$) are definitely due to lithium ethoxide.

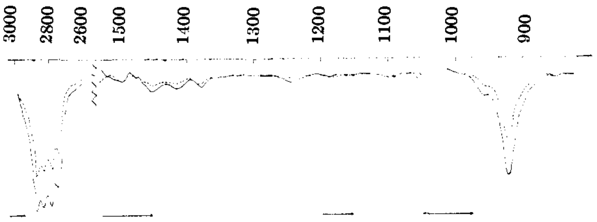

Fig. 1.—Spectrum of ethyllithium in benzene solution: ———, 0.98 *M*; - - - -, 0.56 *M*.

The spectrum of ethyllithium as a Nujol mull is also free of some previously reported bands; the spectrum is shown in Fig. 2A. The most impor-

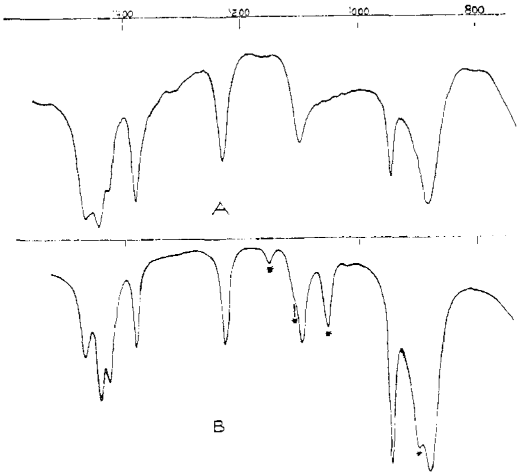

Fig. 2.—Spectrum of ethyllithium as Nujol mull (A) and as a melt (B). Asterisks in B indicate bands probably due to decomposition.

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(6) (a) A. N. Rodinov, D. N. Shigorin, T. V. Talalaeva and K. A. Kocheshkov, *Isvest. Akad. Nauk.* (*Fiz. Ser.*), **22**, 1110 (1958). (b) A. N. Rodinov, V. N. Vasileva, T. V. Talalaeva, E. N. Guryanova and K. A. Kocheshkov, *Dokl. Akad. Nauk. S.S.S.R.*, **126**, 562 (1959). (c) D. N. Shigorin, *Spectrochim. Acta*, **14**, 198 (1959).

(7) V. N. Nikitin, G. V. Rakova and N. V. Mikhailova, *Dokl. Akad. Nauk.*, **124**, 873 (1959).

(8) A. P. Sirnov, D. N. Shigorin, T. V. Talalaeva and K. A. Kocheshkov, *ibid.*, **136**, 634 (1961), also report the spectrum of lithium ethoxide. A few very weak absorptions reported by them are missing in our spectra.

(9) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

tant features are the absence of a band at 1050 cm.$^{-1}$, and the presence of a strong band at 1230 cm.$^{-1}$. Since lithium ethoxide absorbs in the 1050 cm.$^{-1}$ region (momentary exposure of the mull to air results in the appearance of a band there), the mulls would appear to be free of this almost ubiquitous contaminant. The spectra do show a strong absorption at 1098 cm.$^{-1}$, however, so that this band is characteristic of solid ethyllithium or of an impurity as yet unidentified. Since solution spectra prepared from the same solid samples which are used in preparing the mulls show no evidence of decomposition, it is our opinion that the band is indeed due to solid ethyllithium

Spectra were also obtained for ethyllithium melted between salt plates and then allowed to solidify, Fig. 2B. These invariably showed some evidence of decomposition but were otherwise similar to the Nujol spectra. Comparison of a number of melt spectra of varying quality led to identification of bands due to impurities as indicated by asterisks in Fig. 2B.

The effect on the infrared spectra of substituting lithium^6 for natural abundance lithium, already described by West and Glaze,[2] was also observed by us, and with the same result: No apparent shift in frequency (to within 1 cm.$^{-1}$) was observed in any of the bands in the 650–4000 cm.$^{-1}$ region in any of the spectra.

N.m.r. Spectra.—The proton resonance spectrum for an ethyllithium solution in benzene shows a well-separated triplet and quartet characteristic of an A_2X_3 (or A_2B_3) system. First-order analysis of the spectrum yields the parameters

$$\delta_A = 8.12 \pm 0.05 \text{ p.p.m.}$$
$$\delta_X = 5.93 \pm 0.05 \text{ p.p.m.}$$
$$|J_{AX}| = 8.4 \pm 0.1 \text{ c.p.s.}$$

The chemical shifts are referred to the center of the benzene absorption. The large negative internal chemical shift of about −2.19 p.p.m. is to be expected, since the atom joined to the methylene carbon is of low electronegativity.[10] It is, however, slightly larger than one would predict from extrapolation of the trend discussed by Narasimhan and Rogers for ethyl compounds, assuming the electronegativity of lithium to be about 1.0–0.9. Some of the variance may be ascribed to the fact that the methylene carbon is involved in electron-deficient bridge bonding. The observed chemical shift values do not change significantly in the concentration range 0.4–1.2 *M*.

An n.m.r. signal due to the lithium nucleus in solution or in the liquid state has apparently not been previously reported. We have observed the lithium resonance for ethyllithium in benzene solution. It is a surprisingly sharp line; the half-intensity width is of the order of 2 c.p.s. It compares closely in shape with the line due to the 70% hydrated lithium bromide solution in water employed as external standard. It occurs at a chemical shift of −1.00 p.p.m. from this standard. A 7% solution was also employed as external standard, to provide a means of identifying the line due to the sample. The chemical shift observed from this standard was −1.28 p.p.m..

Lithium^7 possesses a nuclear spin of 3/2; its quadrupole moment is sufficiently large so that quadrupolar relaxation should cause appreciable broadening of the resonance line unless the lithium nucleus is located in an environment of high symmetry. Alternatively a rapid change in environment as a result of chemical exchange or other process may produce an averaged field of high symmetry. The existence of a highly symmetric environment for the lithium nucleus seems unlikely. Short of presuming an essentially ionic carbon–lithium bond, no reasonable bonding scheme leading to an environment of higher than trigonal symmetry has occurred to us. Although the occurrence of the lithium resonance in ethyllithium at a lower field than for the aqueous lithium ion gives one pause, it cannot be taken as evidence of ionic character in the alkyls. The effect of the solvating water molecules on the shielding of the lithium ion is undoubtedly very great. Clearly, however, further work on the n.m.r. behavior of the lithium nucleus in various chemical environments is needed.

The absence of an observable spin–spin coupling between lithium and the protons should also be noted. This may be the result of a small coupling constant or may result from rapid exchange of alkyl groups bonded to a particular lithium atom. A noticeable spin–spin coupling is absent also from the proton resonance spectra of other lithium alkyl compounds.[11]

Discussion

In addition to clarifying the spectrum of ethyllithium solutions in the range 650–4000 cm.$^{-1}$, the infrared studies reported here reveal that the absorption at 923 cm.$^{-1}$ due to ethyllithium obeys Beer's law over a wide range of concentrations. If more than one kind of associated species is present in appreciable concentrations in the solutions, therefore, all of the forms present must absorb at the same frequency and exhibit about the same value of extinction coefficient. The 923 cm.$^{-1}$ band is quite intense and was studied thoroughly because of its usefulness as an analytical tool, but less intense absorptions also appear to obey Beer's law over the same range of concentration.[12] The results appear to us to support the argument that a single species predominates in the solutions. The fact that the chemical shifts and coupling constants obtained from the proton resonance spectra do not exhibit significant concentration dependence provides additional support.

Ethyllithium exists as a hexamer and tetramer in the vapor phase at about 90°. It seems reasonable to assume that if a single species is present in the benzene solutions, it is one of these two forms. We have begun a detailed study of the freezing point lowering of ethyllithium solutions, in the hope of improving on previous measure-

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(10) P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 5983 (1960).

(11) C. S. Johnson, M. A. Weiner, J. S. Waugh and D. Seyferth, *ibid.*, **83**, 1306 (1961).

(12) The shoulder at 955 cm.$^{-1}$ and at weak band at 1240 cm.$^{-1}$ were also studied. In addition, it was observed that the relative intensities of the four bands occurring the range 2720–2880 cm.$^{-1}$ are unaffected by concentration.

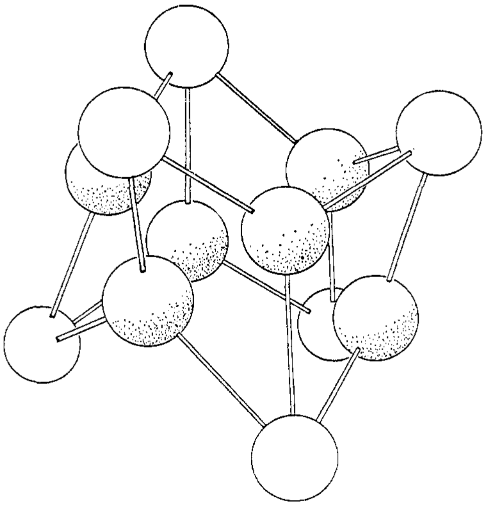

Fig. 3.—Model for proposed structure of ethyllithium hexamer. Stipled spheres represent lithium atoms; blank spheres represent the methylene carbon atoms. The two hydrogens and the methyl group on each carbon are not shown.

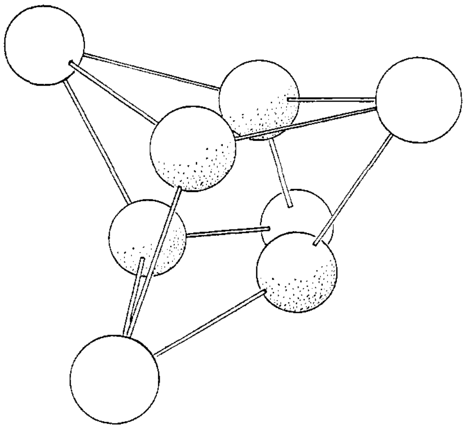

Fig. 4.—Model for proposed structure of ethyllithium tetramer. See caption for Fig. 3.

ments.[4,13] The preliminary measurements obtained to date have yielded values of the association number (apparent molecular weight/formula weight of monomer) which vary from 6.0 to 4.5 in the concentration range 0.03–0.34 molal, with no systematic variation with concentration. The scatter in the values is believed to be the result of some decomposition. Taken together with the previous work done with recrystallized ethyllithium,[4,13a] the molecular weight measurements thus favor the hexamer as the species present in solution, since decomposition (especially if due to reaction with water) would probably result in a lower apparent molecular weight.

The experimental data now available on ethyllithium in the vapor and in solution provide a reasonable basis on which to propose structures for both hexamer and tetramer. One may begin by recognizing that lithium 2s and 2p atomic orbitals will be employed in bonding to the maximum extent permitted by spatial limitations and the number of orbitals available for bonding to lithium.[14] A three-center bonding scheme of the sort which is adequate for describing the structures of aluminum trimethyl dimer or beryllium dimethyl polymer is not satisfactory when applied to the lithium alkyls. It would require that each lithium be bound to two carbons, so that a chain-like structure should result. It is not clear that on this basis only a hexamer or tetramer should possess unusual stability. Furthermore, the appearance potential of Li^+ in the mass spectrum of ethyllithium vapor is particularly large (∼14 e.v.), especially when viewed in relation to the values of the parent $Li_6R_5^+$ and $Li_4R_3^+$ fragments (∼8 e.v.). It may be inferred that the lithium atoms are rather extensively bonded in the polymers and that electron-deficient bonds involving more than three centers are involved.[3]

Consideration of possible bonding schemes has led us to propose structures involving four-center bonds. Models for the structures of hexamer and tetramer are shown in Figs. 3 and 4. Each lithium atom is bonded to three carbon atoms, and *vice versa*. The point group symmetry of the hexamer framework is, ideally, D_{3d}; that of the tetramer framework is T_d. The localized four-center orbitals each involve a carbon sp^3 hybrid orbital and the atomic orbitals of three lithium atoms. While it is not possible to specify the hybridizations of the lithium orbitals, they may be viewed as sp^2 or possibly as containing somewhat more p character. In any event, each lithium atom possesses a vacant atomic orbital in its valence shell. It is important to note that the alkyl groups are located on the periphery of the structure, whereas the lithium atoms form a kind of inner core. The carbon atom is bonded to one bonding center; when the molecule is ionized on electron impact, the alkyl group is lost relatively easily. The appearance of $Li_nR_{n-1}^+$ parent ions in the mass spectrum is thus accounted for. Each lithium atom, on the other hand, is bonded to three different bonding centers. Formation of Li^+ requires, therefore, the rupture of three bonding centers, and the appearance potential for this species is consequently high.

The lithium atoms in the hexamer form a six-membered ring in the chair form. The high energy intermediate in the inversion of ring to the other chair form may be pictured as shown in Fig. 5. The structure is a planar, six-membered ring of lithium atoms joined by three-center bonds. The inversion of the structure through this intermediate may provide a mechanism by which the field about the lithium nucleus attains a high averaged symmetry and by means of which an exchange of alkyl groups amongst the lithium atoms occurs. Although the barrier for such an inversion should be rather high, the inversion rate may be fast enough to account for the observed n.m.r. spectra. The exchange of methyl groups in the aluminum trimethyl dimer, as required to account for the proton resonance spectrum,[15] also appears to

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(13) (a) F. Hein and H. Schramm, *Z. physik. chem.*, **A151**, 234 (1930). (b) K. B. Piotrovsky and M. P. Ronima, *Dokl. Akad. Nauk, S.S.S.R.*, **115**, 737 (1957).

(14) R. E. Rundle, *J. Phys. Chem.*, **61**, 45 (1957).

(15) N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **82**, 248 (1960).

require a rather high energy intermediate. A process analogous to that postulated for the hexamer is also possible for the tetramer.

The distance between adjacent alkyl groups in the tetramer is considerably greater than the corresponding distance in the hexamer. One might speculate that in the absence of any steric interactions between alkyl groups the hexamer is the more stable structure. If this is correct, increased branching of the alkyl groups should cause the hexamer–tetramer equilibrium to shift in favor of the latter. Evidently in the case of ethyllithium the solvent stabilizes the hexamer in solution, whereas in the gas phase the two species are of about the same energy. Methyllithium in the gas phase should exist as essentially all hexamer if the above reasoning is correct.

A complete solid state structure determination has not been carried out as yet on any lithium alkyl. It does appear from the results of a two-dimensional structure study on ethyllithium[16] that the compound exists as a sheet polymer. We have attempted to infer something of the three dimensional structure from the available data. The most that can be said is that a reasonable model can be constructed in accordance with the space group requirements in which each lithium atom is in a nearly trigonal environment of methylene carbon atoms.

The degree of concordance between the proposed structure (hexamer) and the reported dipole moment for ethyllithium[17] requires some discussion. While the hexamer and tetramer frameworks possess centers of symmetry, the over-all symmetry of the molecules is lower (for ethyllithium) because of the fact that the bridging carbons are joined to two hydrogens and one methyl group. From the large negative internal chemical shift observed in the ethyl group proton resonance and simply on the basis of chemical experience, it is reasonable to conclude that the carbon–carbon bond is polar. At the same time, the carbon–carbon and carbon–hydrogen bond moments undoubtedly differ in magnitude. As a result the alkyl group possesses a group moment with components as shown in Fig. 6. The components along the axis cancel in the molecule by reason of symmetry. The other components, however, which may assume various orientations through rotation of the alkyl group about the axis, do not cancel.[18] If the barrier to rotation were quite high and if the position of lowest energy were such that the over-all symmetry of the molecule were D_{3d}, then the moment of the hexamer would be zero. It does not seem at all likely, however, that this should be the case, so that a non-zero moment is to be expected for ethyllithium. It can be seen from this discussion that a lithium alkyl with identical groups attached to the bridging carbon should possess zero dipole moment, assuming that it is in the form of the hexamer or tetramer. Measurement of the dipole moment of *tert*-butyl lithium should thus provide an interesting test case. We hope in the near future to measure the dipole moments of an appropriate series of lithium alkyls.

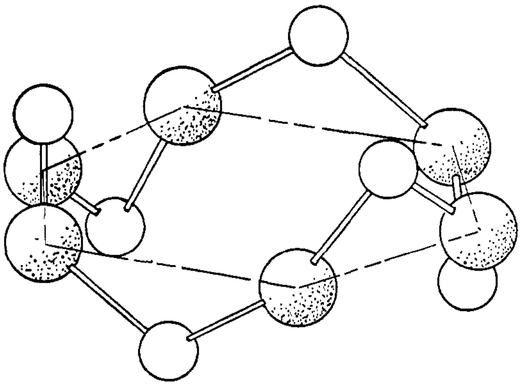

Fig. 5.—Structure of possible high-energy intermediate in the inversion of ethyllithium hexamer. Blank spheres represent the methylene carbon atoms. Stipled spheres represent lithium atoms.

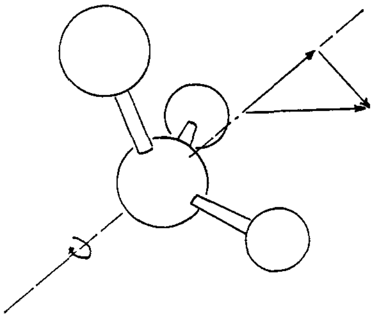

Fig. 6.—Components of ethyl group moment in ethyllithium.

The proposed structures are of some interest with respect to the chemical properties of lithium alkyls in hydrocarbon solvents. The rate of racemization of optically active *sec*-butyllithium in hydrocarbon solvent is sufficiently slow[19] to support the contention that the hexamer (or possibly the tetramer) is quite stable with respect to loss of alkyl groups. The inversion mechanism proposed for exchange of alkyl groups in the polymers would not lead to loss of configuration at the carbon atom.

The lithium atoms in both the hexamer and tetramer possess a vacant orbital and are thus capable of acting as Lewis acids. The solubility of lithium ethoxide in ethyllithium solutions may be due to coördination of the oxygen atom through the vacant lithium orbital. From the fact that the infrared absorptions due to ethyllithium are changed only slightly on addition of ethoxide, it appears possible that the hexameric structure is maintained. In the presence of strong bases, however, such as amines or ethers, the hexamer

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[16] H. Dietrich, *Z. Naturforsch.*, **14b**, 739 (1959).

[17] (a) M. T. Rogers and T. L. Brown, *J. Phys. Chem.*, **61**, 366 (1957). (b) V. N. Vasileva, T. V. Talalaeva, E. N. Guryanova and K. A. Kocheshkov, *Izvest. Akad. Nauk. S.S.S.R.*, 1960, 1549. (c) A. N. Rodinov, V. N. Vasileva, T. V. Talalaeva, D. N. Shigorin, E. N. Guryanova and K. A. Kocheshkov, *Dokl. Akad. Nauk, S.S.S.R.*, **125**, 562 (1959).

[18] The situation encountered here is another instance, albeit a rather complicated one, of internal rotation; J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, Chapter 10.

[19] D. Y. Curtin and W. J. Koehl, *Chem. and Ind.* (*London*), **262** (1960).

structure is probably disrupted in favor of strong bonds to the base molecules, so that one would not expect the lithium alkyls to exist as hexamer or tetramer in basic solvents. Halogen–metal interchange or metalation reactions[20] in hydrocarbon solvents presumably occur through initial coördination of the halogen (or basic atom, in the case of metalations) to the lithium. The reaction following initial coördination may be either the exchange reaction or (in the case of alkyl or aryl halides) coupling.

Acknowledgment.—This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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(20) G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen, London, 1960, pp. 9–17.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON, DELAWARE]

The Mechanism of Oxidation of *p*-Cymene

BY HAROLD BOARDMAN

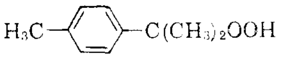
RECEIVED MAY 1, 1961

The kinetics of the oxidation of *p*-cymene, catalyzed by several initiators, has been investigated by measuring the instantaneous rate of oxygen uptake as a function of initiator concentration and by following the rate of hydroperoxide formation to low conversions. The major product of the oxidation, *p*,α,α-trimethylbenzyl hydroperoxide (I), is accompanied by minor amounts of *p*-isopropylbenzyl hydroperoxide (II), *p*-methylacetophenone (III) and 8-*p*-cymenol (IV). Evidence is given for the formation of II and IV in co-oxidation reactions and of I and III in the termination reaction.

It has been known for some time that *p*-cymene can be oxidized with molecular oxygen to give a variety of products, depending upon the experimental conditions. Thus, at temperatures of 140 to 170° in the presence of metal oxides, *p*-toluic acid and *p*-methylacetophenone were isolated from a *p*-cymene oxidate.[1] The use of a lead–manganese acetate catalyst permitted *p*-cymene to be oxidized at about 50° and the oxidate contained cumic acid, 8-*p*-cymenol and *p*-methylacetophenone.[2] The autoxidation of *p*-cymene in an aqueous alkaline medium produced *p*,α,α-trimethylbenzyl hydroperoxide which was identified through its reduction products.[3] Helberger, *et al.*,[4] presented evidence that a primary hydroperoxide, *p*-isopropylbenzyl hydroperoxide, was produced by the autoxidation of *p*-cymene at 60° in sunlight for ten days. Weber[5] was unable to confirm this but found that the ultraviolet-catalyzed oxidation proceeded at 90° to give a mixture of primary and tertiary hydroperoxide.

The object of this work was to make a detailed study of the mechanism of oxidation of *p*-cymene. The oxidations were conducted at temperatures below 85° to avoid initiation of oxidation by the hydroperoxide products. The rate of initiation can then be controlled by the use of initiators with known rates of decomposition.

Under these conditions the major products are: *p*,α,α-trimethylbenzyl hydroperoxide (I) (symbolized as ROOH), *p*-isopropylbenzyl hydroperoxide (II) (symbolized as R′OOH), *p*-methylacetophenone (III) and 8-*p*-cymenol (IV). Under the conditions of these experiments no *p*-methyl-α,α-dimethylbenzyl peroxide was formed.



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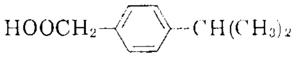
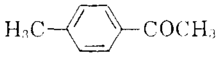
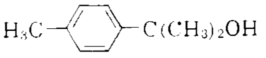


II



III



IV

It was felt that a detailed kinetic study of this oxidation, particularly at low kinetic chain lengths, might indicate how these products are formed. A further objective was to elucidate the nature of the chain terminating step, essentially by comparing rate of oxygen uptake with rate of formation of oxygen-containing products.

Experimental

Materials. *p*-Cymene.—A commercial sample of *p*-cymene was washed with $^1/_4$ portions of concentrated sulfuric acid until the acid layer was clear. It was then washed with 10% sodium hydroxide solution and then with distilled water, dried and fractionally distilled through a 2-ft. glass helices-packed column. The hydrocarbon was stored under a nitrogen atmosphere until used. Ultraviolet analysis indicated it to be >99% pure.

1,1′-Azodicyclohexanecarbonitrile.—This initiator was prepared by dissolving 65 g. of potassium cyanide and 65 g. of hydrazine sulfate in 1,250 ml. of water, adding 600 ml. of dioxane and 98 g. of cyclohexanone and stirring at room temperature for 41 hr. The crystals that formed were filtered and washed with 2 liters of water and 200 ml. of cold ethanol. The crystals were placed in a 4-liter beaker and 1000 ml. of absolute ethanol, saturated with hydrogen chloride gas, was added. The mixture was cooled in an ice bath and a solution of 157 g. of bromine in 1000 ml. of alcohol was added dropwise until the solution remained yellow. The alcohol solution was poured into 4 liters of ice water and the crystals that separated were filtered and recrystallized from 500 ml. of alcohol containing enough water to cause incipient crystallization. After two recrystallizations, 18 g. of white crystals, m.p. 113°, was obtained.

Anal. Calcd. for $C_{14}H_{20}N_4$: N, 22.9; C, 68.9; H, 8.2. Found: N, 21.7; C, 68.6, 68.7; H, 8.1, 8.2.

Potassium Persulfate.—This initiator was used to initiate the oxidation of *p*-cymene in an emulsion system. It has been shown that the rate of decomposition of potassium persulfate in water solution is not affected by the presence of dissolved oxygen[6]; the rate is, however, greatly affected by the presence of dissolved organic materials. Consequently, the rate constant for the decomposition of potas-

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(1) C. E. Sensemann and J. J. Stubbs, *Ind. Eng. Chem.*, **24**, 1184 (1932).

(2) R. C. Palmer and C. H. Bibb, U. S. Patent 2,302,466 (1941).

(3) E. J. Lorand and J. E. Reese, U. S. Patent 2,438,125 (1948).

(4) J. H. Helberger, A. von Rebay and H. Fettback, *Ber.*, **72**, 1643 (1939).

(5) H. Weber, *Angew. Chem.*, **62**, 450 (1950).

(6) P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).