

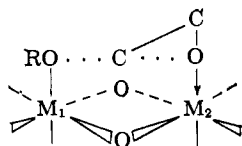
DL-Propylene oxide was polymerized with iron,² zinc,³ and aluminum⁴ catalysts. The crystalline and amorphous fractions were separated.^{2,5} Each was then separately treated with about 50 mole % of ozone in chloroform⁶ followed by lithium aluminum hydride. The dimer glycol fraction was then separated by g.l.c. into the diprimary, primary-secondary, and disecundary isomers⁷ corresponding to head-to-head, head-to-tail, and tail-to-tail structural placements in the original polymer chains. The results are summarized in Table I.

Table I. Head-to-Head Structure and Optical Activity^a of Poly(propylene oxides) from Various Catalysts

Cat.	M.p., deg.	$[\alpha]^{20D}$, deg.	% H-H glycol Exptl. Calcd. ^a	
Zn ³	Amorph.	-4	39	42
Fe ²	Amorph.	-10	33	30
Al ^{4,5}	Amorph.	-18.5	25	13 ^b
KOH	56	-20	10	10
Zn	66	-25	<1	0

^a Calcd. % H-H glycol = $2(25^\circ - [\alpha]^{20D})$. ^b The discrepancy here may arise because the data on optical rotation were from polymer made with aluminum isopropoxide-zinc chloride,⁵ the data on head-to-head structure on polymer from triethylaluminum-water.⁴

In addition to the data on head-to-head irregularities, it is possible to obtain data from D-propylene oxide on the extent of inverted centers⁸ in the amorphous polymer. On the assumption that every optically inverted center entered the chain structurally inverted (*i.e.*, as a head-to-head unit), we can calculate the number of structural irregularities from the optical rotation. The degree of agreement between head-to-head units found experimentally and calculated by this assumption (Table I) strongly supports the conclusion that optical and structural inversion occurs with a 1:1 correspondence. We may, therefore, conclude that the earlier speculation⁵ suggesting that amorphous polymer from optically active monomer arose from racemization of asymmetric centers is incorrect. This also then leads us to reject coordination rearrangement at a single metal atom by an S_Ni mechanism as a reasonable model for this process, but at least two metals, perhaps adjacent, must be involved, a possibility we had pointed out in 1956.⁵ We therefore suggest the following as a partial model for the transition state in coordination-rearrangement polymerization of an epoxide.



(2) M. E. Pruitt and J. M. Baggett, U. S. Patent 2,706,181 (April 12, 1955).

(3) J. Furukawa, T. Tsuruta, R. Sakata, T. Saegusa, and A. Kawasaki, *Makromol. Chem.*, **32**, 90 (1959).

(4) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 486 (1960); *Polymer Letters*, **2**, 1085 (1964).

(5) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956); *J. Polymer Sci.*, **34**, 153 (1959).

(6) A. L. Tumolo and C. C. Price, *J. Am. Chem. Soc.*, **86**, 4691 (1964).

(7) Details are reported in the University of Pennsylvania Ph.D. dissertations of A. L. Tumolo (1963) and R. Spector (1965).

(8) N. S. Chu and C. C. Price, *J. Polymer Sci.*, **A1**, 1105 (1963).

Tsuruta⁹ has presented convincing evidence that the stereoselection for isotactic polymer formation occurs at the coordination step due to asymmetry at the catalyst site, presumably from the nature of the other three ligands at the Lewis acid metal (M).

Vandenberg⁴ has concluded that every ring opening in the polymerization of 2-butene oxide occurs with inversion of configuration at one carbon atom. We¹⁰ have found the same to be true for all the catalysts mentioned in Table I by using *cis*- and *trans*-1,2-deuterioethylene oxides.

We therefore conclude that every ring-opening step in epoxide polymerization by all catalysts we have so far studied proceeds with inversion of configuration at one of the ring carbons, that catalyst sites producing isotactic propylene oxide rings open by highly selective attack at the primary carbon atom, and that they produce isotactic polymer by stereoselection in the coordination step. The catalyst sites in such catalysts which produce amorphous polymer *even from D-monomer* must do so by virtue of relatively nonselective ring opening at either the primary carbon (to put in a D-unit) or at the secondary carbon (to put in a unit inverted both in configuration and structure).

(9) S. Inoue, T. Tsuruta, and N. Yoshida, *Macromol. Chem.*, **79**, 34 (1964).

(10) R. Spector, Ph.D. Dissertation, University of Pennsylvania, 1965.

Charles C. Price, Robert Spector

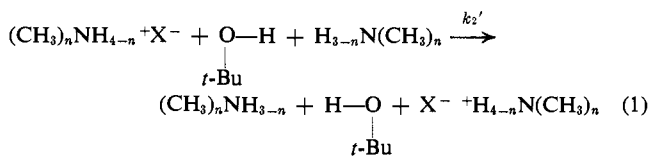
Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104

Received March 27, 1965

Hydrogen-Bonded Structure of Ion Pairs of Ammonium Salts as Deduced from Proton-Exchange Rates

Sir:

We have studied the kinetics of the proton-exchange reaction (eq. 1) in *t*-butyl alcohol, a solvent of fairly



low dielectric constant, at concentrations at which the electrolytes exist largely in the form of ion pairs.¹ This reaction follows second-order kinetics, first order each in ammonium salt and amine. The fact that the rate depends on the first power of the salt concentration precludes a mechanism involving the dissociated ammonium ion because such a mechanism requires that the rate depend on the square root of the salt concentration. The value of the second-order rate constant, k_2' , depends on the nature of both the methyl-substituted ammonium ion and the anion and reveals information about the structure of their ion pairs.

Values of k_2' in *t*-butyl alcohol at 35° are listed in Table I. Second-order rate constants, k_2 ,²⁻⁵ for the

(1) L. Marple and J. Fritz, *Anal. Chem.*, **35**, 1223 (1963).

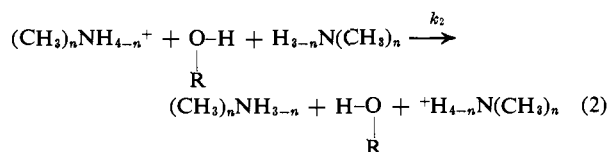
(2) E. Grunwald, P. Karabatsos, R. Kromhout, and E. Purlee, *J. Chem. Phys.*, **33**, 556 (1960).

(3) A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957); A. Loewenstein, *J. Phys. Chem.*, **67**, 1728 (1963).

(4) E. Grunwald, *ibid.*, **67**, 2208 (1963).

(5) E. Grunwald, unpublished work.

analogous reaction (eq. 2) involving dissociated ions in solvents of higher dielectric constant are listed in Table II. The values of k_2 are quite nonspecific,



depending only slightly on the number of methyl groups in the ammonium ion. Furthermore for trimethylammonium ion, the values in water and methanol are almost the same.

Table I. Values of k_2' for Methyl-Substituted Ammonium Salts in *t*-Butyl Alcohol at 35°

Cation	Anion	$k_2' \times 10^{-5},$ $M^{-1} \text{ sec.}^{-1}$	$k_2(\text{H}_2\text{O})/$ $k_2'(t\text{-BuOH})$
$(\text{CH}_3)_3\text{NH}^+$	Cl^-	1.1 ± 0.12	3500
	TFA^-^a	1.8 ± 0.4	2200
	Br^-	5.3 ± 0.7	740
$(\text{CH}_3)_2\text{NH}_2^+$	OTs^-^b	7.0 ± 0.7	560
	Cl^-	270 ± 40	38
	OTs^-^b	310 ± 30	33
CH_3NH_3^+	TFA^-^a	220 ± 20	46
	Cl^-	260 ± 30	23
	OTs^-^b	240 ± 40	25

^a Trifluoroacetate. ^b *p*-Toluenesulfonate.

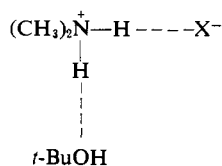
Table II. Values of k_2 for Methyl-Substituted Ammonium Ions in Water and Methanol at 35°^a

Cation	$k_2 \times 10^{-8},$ $M^{-1} \text{ sec.}^{-1}$	Solvent	Ref.
CH_3NH_3^+	6.1	H_2O	2
$(\text{CH}_3)_2\text{NH}_2^+$	10.3	H_2O	3
$(\text{CH}_3)_2\text{NH}^+$	3.9	H_2O	4
$(\text{CH}_3)_3\text{NH}^+$	3.7	MeOH	5

^a Extrapolated from 25° using the activation energies given in ref. 3 and 4.

The values of k_2' in *t*-butyl alcohol are considerably smaller than those of k_2 and show a distinctive dependence on the nature of the reactant. For the mono- and dimethylammonium salts, the values are nearly identical and quite independent of the nature of the anion. For the trimethylammonium salts, the values depend strongly on the nature of the anion and are significantly smaller than those for the mono- and dimethylammonium salts.

These results can be explained adequately by the following theory. In the ion pair, one of the NH protons is hydrogen bonded to the anion; any others are hydrogen bonded to solvent molecules. An example is



Also, an NH proton that is hydrogen bonded to an anion is considerably less reactive than one that is hydrogen bonded to a solvent molecule.

The data in Table I are consistent with this theory. For the mono- and dimethylammonium salts, the values

of k_2' are nearly identical, and the relative rates k_2'/k_2 (relative to water) are in the ratio (1/24):(1/39) or 1.62. This ratio is very close to the ratio of statistical factors, (2/3):(1/2), or 1.33, that would be expected if one of the NH bonds which is reactive in water becomes unreactive in *t*-butyl alcohol. After statistical correction, k_2'/k_2 for both the mono- and dimethylammonium salts is around 1/17. This reduction could be due to a number of factors: the lower dielectric constant, the greater steric bulk of the *t*-butyl alcohol molecule, and the proximity of the anion (which could reduce the acidity of the NH protons).

For trimethylammonium salts, k_2'/k_2 is appreciably smaller than 1/17 and depends strongly on the nature of the anion. These results indicate that the sole NH proton of the cation interacts strongly with the anion (probably through a hydrogen bond). In further support of this theory, the chemical shifts of NH vs. OH protons for the trimethylammonium salts were found to depend on the anion.

The rates of NH-OH proton exchange were measured by n.m.r. spin-echo techniques similar to those described previously.⁶ These rates were measured at electrolyte concentrations between 10^{-3} and 10^{-1} *M* and at a number of acid-base ratios, and they followed good second-order kinetics. These results and further measurements with added common ion salts (to be reported more fully later) have convinced us that the proton exchange involves ion pairs (BH^+X^-) rather than dissociated ions (BH^+).

In conclusion, proton exchange provides a tool for probing the structure of ion pairs formed from ammonium salts. When the solvent is *t*-butyl alcohol and the anion is Cl^- , Br^- , OTs^- , or TFA^- , the anion appears to be hydrogen bonded to just one NH proton of the ammonium cation. Further work is in progress.

(6) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2965 (1964).

Michael Cocivera, Ernest Grunwald
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
Received March 17, 1965

α -Silyl Radicals. The Peroxide-Induced Decarbonylation of Triphenylsilylacetaldehyde

Sir:

The free-radical rearrangement of phenyl in a 1,2-shift from carbon to carbon is well known in certain organic substances,¹ but no work appears extant on the analogous organosilicon systems.² We report here a preliminary result which demonstrates a decided difference between carbon and organosilicon compounds in this regard.

Free-radical decarbonylation of triphenylsilylacetaldehyde (1)^{3,4} with di-*t*-butyl peroxide at 150° yielded *no* rearranged product. Methyltriphenylsilane⁴ was

(1) C. Walling in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 407-412.

(2) However, such rearrangements are known in ionic processes with organosilicon compounds. Cf. C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 434-441.

(3) J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, **28**, 2870 (1963).

(4) All compounds described were satisfactorily characterized by comparisons with known samples or, if new, by combustion analysis and concordant infrared and n.m.r. spectra.