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Carbonium Ions. XIII. Ultraviolet Spectra and Thermodynamic Stabilities of Cycloalkenyl and Linear Alkenyl Cations¹

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The 1,3-dialkylcyclopentenyl cations are half formed from their respective dienes in 33–45% H₂SO₄. The 1,3-dialkylcyclohexenyl cations are half formed around 50% H₂SO₄. The 2,4-dimethylpentenyl and 2,3,4-trimethylpentenyl cations are half formed at 73 and 82% H₂SO₄. There are also characteristic differences in the position of λ_{\max} in the ultraviolet spectra for these three categories of alkenyl cations. The shift of diene:cation ratio with acidity is discussed in relation to acidity functions.

Introduction

This paper is concerned with the ultraviolet spectra of alkenyl cations and the shift of equilibria between diene and alkenyl cation as the acid concentration is varied.

Experimental

The ultraviolet spectra were measured either on a Beckman DU or a Cary 14 spectrophotometer. The solutions for the equilibrium studies were prepared by rapidly pouring 10.0 ml. of the aqueous sulfuric acid onto 0.05 ml. of an acetic acid or ethanol stock solution of the diene. Rapid dispersal of the diene minimizes polymerization.

Optical density readings at λ_{\max} were measured at 15-sec. intervals and the data extrapolated back to zero time. The concentration of cation was calculated directly from the optical density since the diene had no significant absorption at λ_{\max} of the cation. The measurements were conducted at 25.0°. The cations were formed from dienes whose syntheses have been described.³

Discussion

The ultraviolet spectra of the aliphatic alkenyl cations possessed the same general shape, a single nearly symmetrical maximum in the 300 m μ region, a minimum around 250 m μ , and a monotonic increase from 240 to 220 m μ . Table I summarizes the values of λ_{\max} and log ϵ .

TABLE I
ULTRAVIOLET SPECTRA OF ALKENYL CATIONS

Cation	λ_{\max} , m μ	log ϵ
1,3-Dimethylcyclopentenyl	275	4.04
1-Ethyl-3-methylcyclopentenyl	278	4.07
1-Isopropyl-3-methylcyclopentenyl	280	4.03
1,3,4,4,5-Pentamethylcyclopentenyl	288	4.01
1,2,3,4,4-Pentamethylcyclopentenyl	299	(4.06) ^a
1,3,4,4,5,5-Hexamethylcyclopentenyl	291	4.13
1,2,3,4,4,5-Hexamethylcyclopentenyl	301	(4.14) ^a
1,3,5,5-Tetramethylcyclohexenyl	314	3.96
1-Ethyl-3,5,5-trimethylcyclohexenyl	318	4.05
1,5,5-Trimethylcyclohexenyl	319	>(3.7) ^b
1-Phenyl-3,5,5-trimethylcyclohexenyl	411	4.65
2,4-Dimethylpentenyl	305	4.03
2,3,4-Trimethylpentenyl	307	3.98

^a The n.m.r. spectra indicated that these cations were quantitatively formed from the preceding cation; log ϵ was calculated on this basis. ^b Accompanying this band is a band with λ_{\max} at 409 m μ (log ϵ 3.4). The 409 m μ band was unchanged between 70 and 96% H₂SO₄ and is suspected as being due to a dienyl cation formed during the process of solution (see footnote 17 of ref. 3).

With the cyclopentenyl and cyclohexenyl cations, there was little doubt about the source of the ultraviolet spectra since the cations were completely stable in 96% H₂SO₄ and the n.m.r. spectra contained only

(1) This research was supported in part by a grant from the National Science Foundation. Grateful acknowledgment is hereby made of this support.

(2) Recipient of a Fellowship sponsored by Shell Companies Foundation.

(3) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

bands due to the cations. It is entirely another matter with linear alkenyl cations. The ultraviolet and equilibrium studies of 2,4-dimethylpentenyl and 2,3,4-trimethylpentenyl cations represent the only data on linear alkenyl cations to which we attach some confidence out of large numbers of such cations examined.

The n.m.r. spectra were reported for the 2,4-dimethylpentenyl and the 2,3,4-trimethylpentenyl cations.³ Although the bands of the cations were sharp and well resolved, the spectra contained background comparable in area to the bands of the cation. This background resembled the n.m.r. spectra of the dimeric dienes in 96% H₂SO₄, and it is thought that it can ultimately be eliminated by improved techniques. However, at present, additional evidence is required to demonstrate that the ultraviolet spectra and equilibrium studies represent valid measurements on the monomeric cations. Three such tests have been devised and are described in the following three paragraphs.

It has been our experience that in every case where the carbonium ion was stable and its presence demonstrated by *i*-factors and/or n.m.r. spectra, the *carbonium ion formed immediately* from its alcohol, diene, or alkene.⁴ It was thus concluded that any measurably

TABLE II

TESTS OF EQUATION 3

H ₂ SO ₄ , %	log c_B/c_{BH^+}	$-H_R + \log a_{H_2O}$	pK (eq. 3)
	Azulene-H ⁺ , λ 352 m μ		
	+1.3	0.70	-2.0
10	+0.74	1.28	-2.02
15	+ .26	1.86	-2.12
20	- .33	2.46	-2.13
25	- .98	3.10	-2.12
30	-1.7	3.82	-2.1
35			
	2-Anisylbornene-H ⁺ , λ 384 m μ		
25	+1.7	2.46	-4.2
30	+1.36	3.10	-4.46
35	+0.76	3.82	-4.58
40	0	4.55	-4.55
45	-0.82	5.32	-4.50
50	-1.4	6.14	-4.7
	2,4,6-Trimethoxyacetophenone-H ⁺ , λ 400 m μ		
35	+1.0	3.82	-4.8
40	+0.15	4.55	-4.70
45	-0.55	5.32	-4.77
50	-1.2	6.14	-4.9
	1-Phenyl-3,5,5-trimethylcyclohexenyl cation, λ 411 m μ		
45	+1.12	5.32	-6.44
50	+0.20	6.14	-6.55
55	-0.40	7.06	-6.64

(4) 2-Phenylborneol required 20 sec. to half form the 2-phenylbornyl cation (ref. 5). This may be an exception although the structure of the cation has not been unequivocally demonstrated.

TABLE III
 EQUILIBRIUM DATA FOR CYCLOALKENYL CATIONS

Cation	Relative optical densities ^a								H ₂ SO ₄ , % ^b	pK (eq. 4)
	H ₂ SO ₄ , % 25	30	35	40	50	60	80	96		
1,3-Dimethylcyclopentenyl		15	31	45	67	82	100	100	35 ^c	-1.9
1-Ethyl-3-methylcyclopentenyl	11	15	24	37	85	96	100	100	42	-2.4
1-Isopropyl-3-methylcyclopentenyl			19	35	78	97	100	100	42	-2.4
1,3,4,4,5,5-Hexamethylcyclopentenyl	18	36	59	80	97	100	100	100	33	-1.8
1,3,5,5-Tetramethylcyclohexenyl			7	53	85	100	100	100	50	-3.2
	H ₂ SO ₄ , %		70	75	80	85	90	96		
1,5,5-Trimethylcyclohexenyl				23	50	82	100	100	80	-6.8
2,4-Dimethylpentenyl			5	61	89	96	100	100	73	-5.9
2,3,4-Trimethylpentenyl				5	40	84	100	100	82	-7.1

^a Measured at λ_{\max} of the cation and extrapolated to zero time. ^b At which $c_{R^+} = c_{diene}$. ^c See discussion in text for an explanation of the choice of this number.

slow formation of absorption around 300 m μ was the result of various combinations of polymerization, rearrangement, and hydride transfer. The 2,4-dimethylpentenyl and 2,3,4-trimethylpentenyl cations met this first test in that they formed completely within 10 sec. from their corresponding dienes.

A second test has been devised for these cations which can be quantitatively formed only in dilute solutions of the order of 10⁻⁵ molar. If the monomeric cation is under observation, its decomposition in the case of tertiary alkenyl cations will proceed by alkylation of the diene by the alkenyl cation.³ This reaction will appear to be kinetically second order in cation concentration. Actually it is first order in cation and first order in diene, but these are in rapid and reversible equilibrium. This test was applied by determining the variation in the initial rates of disappearance, $-dc_{R^+}/dt$, as a function of c_{R^+} . Only when this initial rate was exactly proportional to $(c_{R^+})^2$ over at least a five-fold variation in c_{R^+} was the spectrum assigned to the monomeric cation. The two linear pentenyl cations met this test.

A third test rested on evidence that protonation of hydrocarbons follows eq. 1

$$d(H_R - \log a_{H_2O}) = d(\log c_B/c_{BH^+}) \quad (1)^b$$

eq. 2 (discussed in the following section)

$$dH_0 = d(\log c_B/c_{BH^+}) \quad (2)$$

or exhibit an intermediate behavior. The linear alkenyl cations all had R^+ :diene ratios equal to unity at H₂SO₄ concentrations of 75% or greater and in this region there is not much difference between dH_0 and $d(H_R - \log a_{H_2O})$. The point is that the protonation data should approximately fit eq. 1 and/or 2 and the two linear pentenyl cations met this test.

One of the cyclohexenyl cations, the 1,5,5-trimethylcyclohexenyl cation, was not stable enough to obtain n.m.r. spectra. Confidence in the data for this cation rested on the above three tests.

Thermodynamic Stabilities.—A line of reasoning led to the expectation that protonations of arylalkenes would follow eq. 1 and its integrated form

$$H_R - \log a_{H_2O} = pK + \log c_B/c_{BH^+} \quad (3)^b$$

The initial experimental test was limited to 45–96% H₂SO₄. New data in Table II on the protonation of azulene, 2-anisylbornene, and 2,4,6-trimethoxyacetophenone⁶ extended the experimental test throughout most of the range of H₂SO₄ concentrations. From this work, it might be inferred that protonation on carbon would fit eq. 1 and 3. Such a simplified view was quickly dispelled by the work of Schubert and Quacchia⁷ and Kresge and co-workers,⁸ who showed

(5) N. Deno, P. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).

(6) In the n.m.r. spectrum of protonated 2,4,6-trimethoxyacetophenone, the aromatic hydrogens did not appear, indicating that they were rapidly exchanging with the solvent and that protonation was taking place on carbon.

that in the protonation of 1,3,5-trihydroxybenzene and its methyl ethers, values of $d \log c_B/c_{BH^+}$ ranged from 0.8 of dH_0 for the trihydroxy compound up to 1.6–1.8 of dH_0 for the trimethoxy compound. The n.m.r. spectra indicated that all of these compounds protonate on carbon. Values of $d \log c_B/c_{BH^+}$ intermediate between dH_0 and $d(H_R - \log a_{H_2O})$ were found for the protonation of indoles and pyrroles by Hinman and Whipple.⁹ Again the n.m.r. spectra indicated protonation on carbon.^{9,10}

The protonation equilibria between aliphatic dienes and alkenyl cations fit eq. 2 and its integrated form

$$H_0 = pK + \log c_B/c_{BH^+} \quad (4)$$

more closely than they fit eq. 1 and 3. The optical density data are briefly summarized in Table III along with the % H₂SO₄ at which c_B/c_{BH^+} is unity and the pK calculated by eq. 4.¹¹ Although in most cases, the alkenyl cations are in equilibrium with more than one diene,¹² this has very little effect on the fit of the data with eq. 3 or 4 as can be demonstrated by making the calculations for a hypothetical case of two dienes with various differences in pK.

The data were more difficult to interpret in the case of 1,3-dimethylcyclopentenyl cation. Between 96 and 50% H₂SO₄, there is a steady decrease in optical density

TABLE IV

RATES OF DESTRUCTION OF 1,3-DIMETHYLCYCLOPENTENYL CATION

H ₂ SO ₄ , %	(d(O.D.)/dt) ^a × 10 ⁴	k_2^b
28.3	0.9	...
33.3	5.2	5.4×10^2
35.7	9.2	6.1×10^2
39.6	4.2	...
46.0	1	...

^a This is the rate of change of the optical density at λ_{\max} in respect to time (sec.) at the initial time of mixing. ^b Calculated from the equation $dc_{R^+}/dt = k_2(c_{R^+})(c_{diene})$. The units are l. moles⁻¹ sec.⁻¹. The c_{R^+} was assumed to be directly proportional to optical density, and any absorption due to the polymeric cations produced was ignored. Using the same basis for calculation, k_2 for the 1,3,5,5-tetramethylcyclohexenyl cation was 110 and k_2 for the 1,3,4,4,5,5-hexamethylcyclopentenyl cation was 116.

(7) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **84**, 3778 (1962).

(8) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962).

(9) R. L. Hinman and E. B. Whipple, *ibid.*, **84**, 2534 (1962); R. L. Hinman and J. Lang, *Tetrahedron Letters*, **21**, 12 (1960); E. B. Whipple, Y. Chiang, and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 26 (1963).

(10) R. J. Abraham, E. Bulloch, and S. S. Mitra, *Can. J. Chem.*, **37**, 1859 (1959).

(11) The fit of the data with eq. 4 is presented in detail mainly in the Ph.D. Thesis of James D. Hodge, Pennsylvania State Univ., 1963. Data for the two 1-alkyl-3-methylcyclopentenyl cations will appear in detail in the Ph.D. Thesis of Norman Friedman.

(12) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2995 (1963).

which is interpreted to be a decrease in extinction coefficient of the cation. The sharp decrease in optical density from 40 to 30% H_2SO_4 is regarded as the true shift in equilibrium from BH^+ to B. Supporting this viewpoint are the rates of decomposition which

maximize at 35% acid (Table IV), the point at which c_B/c_{BH^+} equal unity, as required for a bimolecular decomposition path.³

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Ionization Rates of Weak Acids. I. Base-Catalyzed Proton Exchange between Toluene and Tritiated Dimethyl Sulfoxide

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The base-catalyzed hydrogen isotope exchange between toluene and tritiated dimethyl sulfoxide has been carried out using potassium *t*-butoxide at temperatures ranging from 23.5 to 80°. The reaction is first order in isotope concentration and proceeds by ionization, followed by abstraction of tritium from the solvent. The reaction shows marked similarities to olefin double bond isomerization carried out in the same media and is being introduced as a simple technique for measuring the rate of ionization of very weak acids.

Introduction

The discovery that dimethyl sulfoxide exchanges protons with weakly acidic hydrocarbons under the influence of potassium *t*-butoxide² has opened a new area for the study of hydrocarbon acidity. Isotopic proton exchange has been used for a number of years for the measurement of hydrocarbon acidity,³ but except for a few cases^{4,5} this technique has been limited to substrates of $\text{p}K_a < 30$. The use of tritiated dimethyl sulfoxide and potassium *t*-butoxide in conjunction with a radio-assaying gas chromatograph now makes possible the measurement of the relative acidity of hydrocarbons of $\text{p}K_a \sim 40$.

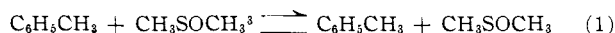
The first paper in this series gives the results for the exchange between toluene and tritiated dimethyl

sulfoxide and the following paper reports the results for exchange with a number of polyalkylbenzenes.

Results

The results of all the kinetic experiments are shown in Table I. The reported first-order rate constant is the slope of the line obtained from equation 4. From these and subsequent experiments,⁶ the precision of a single kinetic determination was found to be about $\pm 10\%$.

From the data shown in Fig. 1, it is clear that, over the temperature range studied, the exchange of toluene with tritiated dimethyl sulfoxide (eq. 1) is first order according to the general equation for isotope exchange^{7,8}



(eq. 2). If, as in the present work, dimethyl sulfoxide

$$\text{rate} = R = \frac{(T)(D)}{\alpha(T) + \beta(D)} \frac{1}{t} \ln \left(1 - \frac{X_t}{X_\infty} \right) \quad (2)$$

T = concentration of toluene

D = concentration of dimethyl sulfoxide

α = kinetic isotope effect in forward direction

β = kinetic isotope effect in reverse direction

X_t = specific activity of toluene at time (t), per reactive hydrogen

X_∞ = specific activity of toluene at equilibrium, per reactive hydrogen

is in large excess, eq. 2 reduces to

$$R = \frac{(T)}{\beta t} \ln \left(1 - \frac{X_t}{X_\infty} \right) \quad (3)$$

which can be rearranged to give

$$\ln \left(1 - \frac{X_t}{X_\infty} \right) = \frac{R\beta}{(T)} (t) \quad (4)$$

A plot of $\ln \left(1 - \frac{X_t}{X_\infty} \right)$ vs. time should then give a straight line.

No attempt has been made to measure the isotope effect β but the ratio of α to β was determined by two independent methods. First, the distribution of tritium at equilibrium was determined and second, the rate of the reverse reaction was measured by exchanging tritiated toluene with unlabeled dimethyl sulfoxide. The ratio α/β for K_{eq} is 1.49 and that for k_f/k_r

(6) For part II, see J. E. Hofmann, R. J. Muller, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 3002 (1963).

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(8) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press, New York, N. Y., 1960.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR PROTON EXCHANGE IN TOLUENE AT DIFFERENT TEMPERATURES

Expt. ^a	Temp., °C.	Toluene concn., moles/l.	Base concn., moles/l.	First-order slope, sec. ⁻¹
1	23.5	0.35	0.56	1.7×10^{-4}
2	30.0	.35	.56	2.7×10^{-4}
3	55.0	.35	.56	2.9×10^{-3}
4	80.0	.35	.56	2.2×10^{-2}
5	30.0	.125	.56	3.2×10^{-4}
6	30.0	.250	.56	3.2×10^{-4}
7	30.0	.375	.48	3.3×10^{-4}
8	30.0	.375	.32	3.1×10^{-4}
9	30.0	.375	.16	1.7×10^{-4}
10	30.0	.375	.08	9.1×10^{-5}
11	30.0	.375	.56	3.0×10^{-4}
12 ^b	55.0	.375	.56	2.0×10^{-3}

^a Experiments 1-4 employed a stock solution of 0.56 M KO*t*-Bu in DMSO which was shown in subsequent work⁶ to exhibit, at standard conditions of 30.0° and 0.56 M base, an average first-order slope for 15 experiments of 2.80×10^{-4} sec.⁻¹. Experiments 5-11 employed a similar stock base-solvent solution whose average first-order slope for 6 determinations was 3.16×10^{-4} sec.⁻¹. ^b This experiment was performed using unlabeled dimethyl sulfoxide and toluene having an initial specific activity in the methyl group of 0.0225 mc./mmole.

(1) Summer employee of Esso Research & Engineering Co. (1962).

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(4) (a) A. Streitwieser, Jr., *et al.*, *J. Am. Chem. Soc.*, **84**, 244 (1962); (b) **84**, 249 (1962); (c) **84**, 254 (1962).

(5) (a) A. I. Shatenshtein, *et al.*, *Tetrahedron*, **18**, 95 (1962); (b) *Dokl. Akad. Nauk SSSR*, **79**, 479 (1951).