

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## Electronegativity of Substituents and Nuclear Magnetic Resonance Spectra of Norbornene Derivatives

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The magnitudes of coupling constants between protons on vicinal saturated carbon atoms vary significantly with changes in the electronegativity of adjacent substituents. This effect has been demonstrated in a number of 5-*endo*-2-norbornenyl derivatives (I). The internal chemical shifts for the same protons also depend on the substituent electronegativities. Contrary to the literature, vinyl and ethyl derivatives are found not to be suitable models for the estimation of these coupling constant and internal chemical shift effects, respectively. Additional features of the nuclear magnetic resonance spectra of compounds I are analyzed.

Coupling constants  $J$  between protons on vicinal carbon atoms C<sub>1</sub>H<sub>1</sub>–C<sub>2</sub>H<sub>2</sub> depend not only on the dihedral angle  $\phi$  between the C<sub>1</sub>H<sub>1</sub>C<sub>2</sub> and C<sub>1</sub>C<sub>2</sub>H<sub>2</sub> planes,<sup>3</sup> but also on the electronegativity of substituents X, CH–CHX.<sup>4–12</sup> The large variation of  $J$  with dihedral angle, a  $\cos^2 \phi$  function, gives the very familiar Karplus curve.<sup>3</sup> The effect of substituent electronegativity on  $J$ , although first noted many years ago,<sup>4</sup> is much less generally appreciated. For simple aliphatic molecules this electronegativity variation is small,<sup>4</sup> but for vinyl compounds the effect can be of comparable magnitude to that of a change in geometry.<sup>5–8</sup> For more complicated aliphatic molecules structural distortions due to the bulk of substituents tend to obscure the electronegativity effect.<sup>9,11</sup> This is especially true for cyclopropanes, which, because of the quasi-double bond character of the carbon–carbon linkages, might be expected to be relatively sensitive to the electronegativity effect. Although significant variations in coupling constants of polysubstituted cyclopropanes have been found, no direct correlation with electronegativity is yet possible with the compounds studied.<sup>9,12a</sup>

To investigate the effect of substituent electronegativities on coupling constants in more complicated aliphatic systems, rigid compounds of known and fixed geometry are needed. We report here on a series of *endo*-Diels–Alder adducts I of cyclopentadiene and various dienophiles. While this work was in progress, Williamson described the results of a similar study on the adducts II of hexachlorocyclopentadiene.<sup>12</sup> The two investigations are complementary and both demon-

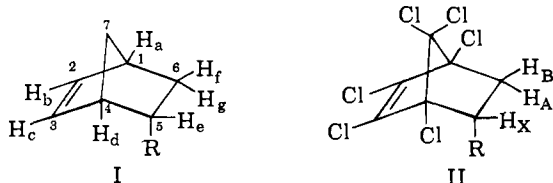
strate the dependence of  $J$  on electronegativity. We here extend and modify some of the conclusions of the earlier investigation.

### Results

**Analysis of N.m.r. Spectra.**—Desired features of the spectra of 5-*endo*-substituted 2-norbornenes (I) were analyzed by first-order theory. Typical spectra, that of the chloro compound (I, R = Cl) and of the cyano compound (I, R = CN) are given in Fig. 1. The spectrum of the nitro compound (I, R = NO<sub>2</sub>) has been published as part of a study of norbornene derivatives.<sup>13</sup> The olefinic hydrogens H<sub>b</sub> and H<sub>c</sub> and the broad bridgehead proton peaks H<sub>a</sub> and H<sub>d</sub> can readily be discerned in the spectra. One of these resonances comes at a position very close to that of the bridgehead protons of norbornene (I, R = H) and is assigned H<sub>a</sub> on this basis. The other bridgehead resonance, H<sub>d</sub>, is shifted downfield. These assignments are reinforced by a quantitative assessment of the electronegativity effect of the substituent R discussed below. Both *exo* protons at C-5 and C-6 (H<sub>e</sub> and H<sub>f</sub>) are deshielded—they lie approximately in the plane of the magnetically anisotropic double bond<sup>13</sup>—and the resonances of both can be distinguished from others (H<sub>g</sub> and the C-7 methylene group) in the molecules. H<sub>e</sub> is further deshielded by the substituent R. The observed chemical shifts are summarized in Table I.

First-order analysis yielded the values of the nonzero coupling constants describing the spin–spin interactions of hydrogens H<sub>a</sub>, H<sub>e</sub>, H<sub>f</sub>, H<sub>g</sub>, and H<sub>d</sub>; namely,  $J_{ef}$ ,  $J_{fg}$ ,  $J_{de}$ ,  $J_{eg}$ , and  $J_{af}$ . With one exception, the interaction of H<sub>e</sub> with H<sub>d</sub> and with H<sub>g</sub> gave rise to a triplet. (The exception (I, R = CH<sub>2</sub>=CHSO<sub>2</sub>) gave four lines for H<sub>e</sub>, a pattern typical of the X part of an ABX spectrum.) The triplet usually observed for proton H<sub>e</sub>—an apparent A<sub>2</sub>X spectrum—is due to the fortuitous near identity of  $J_{eg}$  and  $J_{de}$ . It is *not* a “deceptively simple spectrum”<sup>14</sup>; the requirements for the latter<sup>14</sup> are not met in this system:  $J_{dg} \cong 0$  and the chemical shift difference between protons H<sub>g</sub> and H<sub>d</sub> is relatively large, *e.g.*, at least 30 c.p.s. for I, R = Cl (Fig. 1). Actually,  $J_{de}$  and  $J_{eg}$  are slightly different, but the resolution available was insufficient to distinguish them; Table II lists only their average,  $\frac{1}{2}(J_{de} + J_{eg})$ . For each substituent R in Tables I and II, electronegativities  $E_R$ <sup>15</sup> are given.

In some cases the internal chemical shifts between H<sub>b</sub> and H<sub>c</sub> were sufficient (~10–15 c.p.s.) to permit observation of a typical eight-line multiplet (Fig. 1) in the olefinic region; it consisted of an AB spectrum, each line of which was again split into two by coupling to the vicinal bridgehead proton, H<sub>b</sub> by H<sub>a</sub> and H<sub>c</sub> by H<sub>d</sub>. The results are included in Tables I and II. It



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(12a) NOTE ADDED IN PROOF.—Such correlations have now been reported: K. L. Williamson, C. A. Lanford, and C. R. Nicholson, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

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TABLE I  
 CHEMICAL SHIFTS OF 5-endo-SUBSTITUTED NORBORNENE DERIVATIVES, C.P.S.

I, R =	$E_R$	$1/2(H_b + H_c)$	$H_d$	$H_a$	$H_e$	$H_f$	$H_e - H_f$	$H_e - H_d$
OOCCH <sub>3</sub>	3.72	366	187	170	310	125.5	184.5	123
NO <sub>2</sub> <sup>a</sup>	3.70	368	212	180	296	(128) <sup>b</sup>	(168) <sup>b</sup>	84
Cl	3.25	370	185.5	173.5	268	135	123	72.5
Br	2.96	369	186	169	254	135	119	68
SO <sub>2</sub> CH=CH <sub>2</sub>	2.94	365	193	179	211	124	87	18
C <sub>6</sub> H <sub>5</sub>	2.75	357	179sh	173.5	199	128	71	20
COCH <sub>3</sub>	2.70	351	187	169	172	...	...	-15
CHO	2.69	364	192	174.5	(176) <sup>b</sup>	112	(64) <sup>b</sup>	(-16) <sup>b</sup>
COOH	2.60	362	191	...	179	123	56	-12
COOC <sub>2</sub> H <sub>5</sub>	2.55	360	189	171	171	110	61	-18
CN	2.49	375	192	179	167	127	42	-25
H	2.1	357.5	171	171	(96) <sup>b</sup>	(96) <sup>b</sup>	0	(-73) <sup>b</sup>

<sup>a</sup> Ref. 13. <sup>b</sup> Estimated approximately.

 TABLE II  
 COUPLING CONSTANTS IN 5-endo-SUBSTITUTED NORBORNENE DERIVATIVES, C.P.S.

I, R =	$E_R$	$J_{ef}$	$1/2(J_{eg} + J_{de})$	$J_{fg}$	$J_{af}$	$\Sigma J_{de} + J_{ef} + J_{eg}$	$J_{be}$	$(J_{ab}, J_{ed})$
OOCCH <sub>3</sub>	3.72	7.9	3.25	..	3.5	14.4	5.4	2.9, 3.0
NO <sub>2</sub> <sup>a</sup>	3.70	7.8	3.9	..	..	15.6	...	...
Cl	3.25	8.2	3.5	12.0	3.75	15.2	5.6	2.8, 3.0
Br	2.96	8.2	3.45	12.5	4.0	15.1	5.3	3.0, 3.0
SO <sub>2</sub> CH=CH <sub>2</sub>	2.94	8.7	3.85 <sup>c</sup>	..	3.3	16.4	...	...
C <sub>6</sub> H <sub>5</sub>	2.75	8.9	3.7	10.4	3.7	16.2	...	...
COCH <sub>3</sub>	2.70	...	.. <sup>d</sup>	..	..	..	...	...
CHO	2.69	8.7	.. <sup>d</sup>	12.0	3.5	..	5.6	2.4, 2.5
COOH	2.60	8.5	4.0 <sup>d</sup>	11.6	3.4	16.5	5.7	2.5, 2.6
COOC <sub>2</sub> H <sub>5</sub>	2.55	8.9	4.1 <sup>d</sup>	..	3.5	17.1	5.7	2.5, 2.6
CN	2.49	9.2	3.6	11.5	3.5	16.4	5.7	2.9, 2.5
H <sup>b</sup>	2.1	...	..	..	..	..	5.8	2.95, 2.95

<sup>a</sup> Estimated from the published spectrum, ref. 13. <sup>b</sup> Values determined by analysis of the <sup>13</sup>C-H patterns, ref. 19; Pauling electronegativity used. <sup>c</sup> Individual values observable here: 3.0 and 4.7 c.p.s. <sup>d</sup> For R = COR', M. Green and E. A. C. Lueken (*Helv. Chim. Acta*, **45**, 1870 (1962)) indicate values of 3.5-4.0 c.p.s. for  $J_{de}$ .

was not possible to distinguish between  $H_b$  and  $H_c$  and only the position of the center of gravity of the olefinic multiplet is reported. This position is structure de-

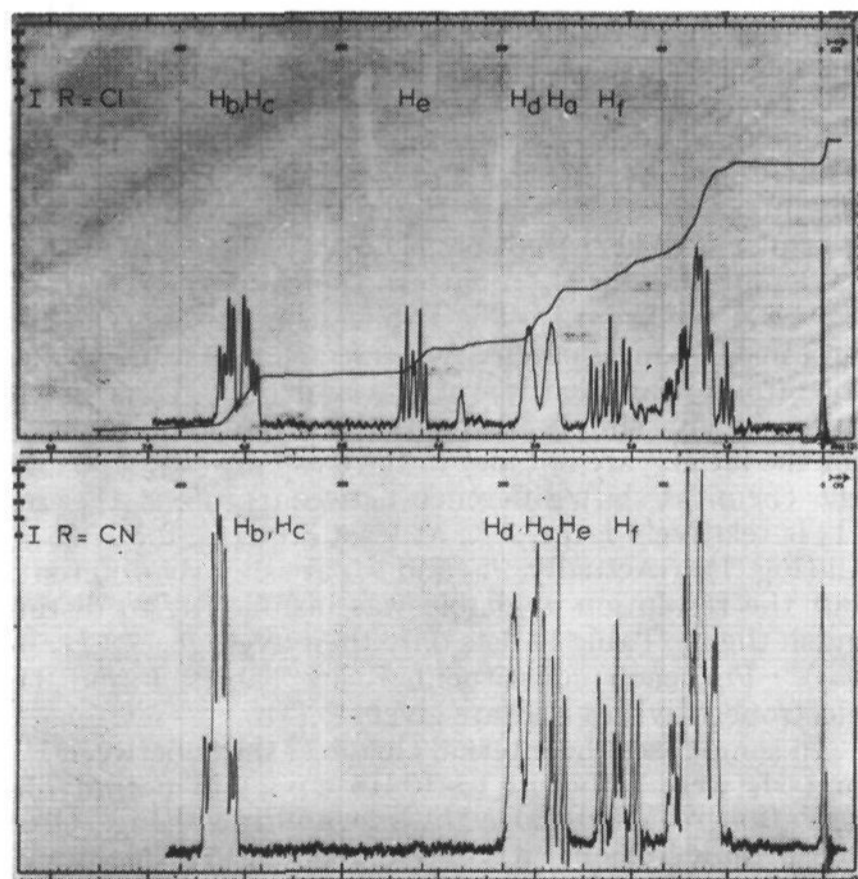


Fig. 1.—N.m.r. spectra of I, R = Cl (top), and I, R = CN (bottom).

pendent (Table I), but the variations, if any, of the coupling constants (Table II) with structure were within the limits of experimental error of measurement.

## Discussion

**Chemical Shifts.**—The differences in chemical shifts between *exo* protons at C-5 and C-6 ( $H_e$  and  $H_f$ ) gave a good correlation with substituent electronegativities ( $E_R$ ), independent of anisotropy effects<sup>16</sup> (Fig. 2).

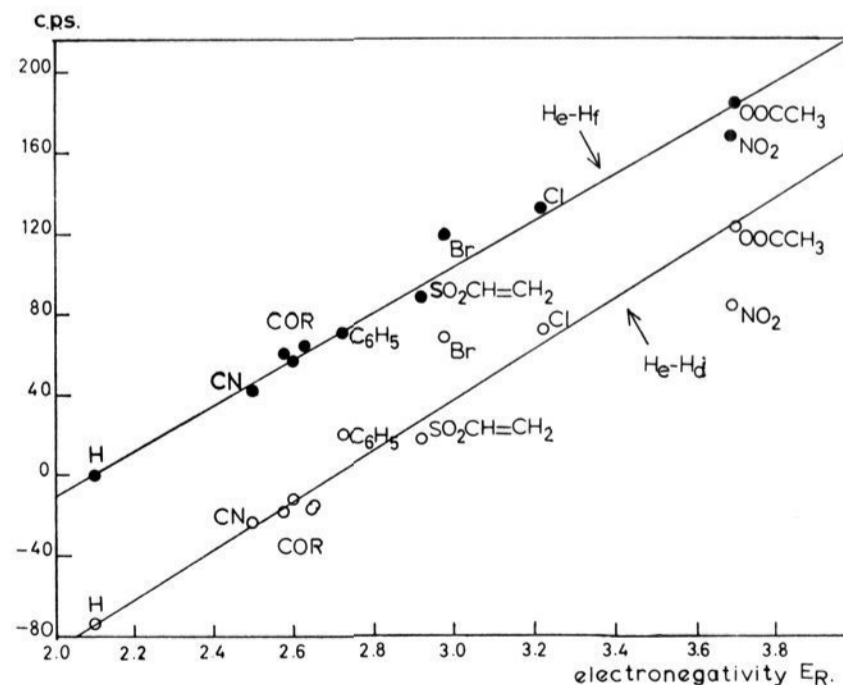


Fig. 2.—Dependence of internal chemical shifts  $H_e - H_f$  and  $H_e - H_d$  on the electronegativity of substituents.

An analogous plot of  $\Delta\delta(H_e - H_d)$  with electronegativity gave only a slightly less satisfactory correlation. Williamson<sup>12</sup> observed for the similar compounds, II, that the electronegativity effect was dependent on azimuthal angle. Table III lists the slopes of the published correlation lines for compounds II<sup>12</sup> and I.

(16) See footnote 28, ref. 12.

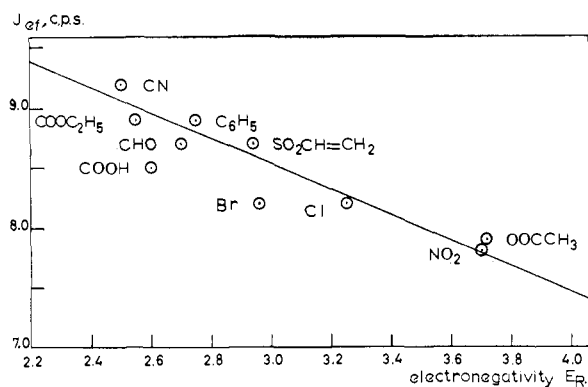


Fig. 3.—Variation of the coupling constant  $J_{ef}$  with the electronegativity of substituents.

Using his results, Williamson calculated the slope for ethyl derivatives, allowing for rotational averaging. The estimate so obtained agreed rather well with the experimental value, 89 c.p.s./ $E_R$  unit.<sup>15</sup> Unfortunately, this agreement is fortuitous. The slope of  $H_e - H_f$  is much higher than  $H_X - H_B$  despite the fact that both have  $\phi = 0^\circ$ , indicating that the many chlorine atoms in compound II attenuate the electronegativity effect of R. Calculations for ethyl derivatives using results for compound I following Williamson's procedure would give results much larger than found experimentally. We agree with Williamson that substituent electronegativity shifts probably depend on azimuthal angle; further experimental examples are needed to show what additional factors are involved.

TABLE III

VARIATION OF ELECTRONEGATIVITY EFFECT WITH AZIMUTHAL ANGLE

Compound	$\phi = 0^\circ$	$\phi \cong 40^\circ$	$\phi = 120^\circ$
	( $H_X - H_B$ ) or ( $H_e - H_f$ )	( $H_e - H_d$ )	( $H_X - H_A$ )
II <sup>12</sup>	64 c.p.s./ $E_R$ unit	...	97 c.p.s./ $E_R$ unit
I	105 c.p.s./ $E_R$ unit	120 c.p.s./ $E_R$ unit	...

None of the other chemical shifts listed in Table I varies in a regular way with  $E_R$ . Erratic shifts, evidently due to substituent anisotropy effects, can be noted. This is especially true for  $R = NO_2$ .<sup>15,17</sup>

**Coupling Constants.**—Correlation of the magnitude of coupling constants with  $E_R$  was observed for  $J_{ef}$  (Fig. 3), for  $\frac{1}{2}(J_{eg} + J_{de})$ , and for  $\Sigma J_{ef} + J_{de} + J_{eg}$  (Fig. 4). These results are in accord with previous investigations; comparisons with literature results

TABLE IV

VARIATION OF VICINAL COUPLING CONSTANTS WITH SUBSTITUENT ELECTRONEGATIVITIES

System	$\alpha^a$	$J_0^a$	Ref!
$CH_3CH_2X$	0.40	8.4	4 (cf. 10)
$(CH_3)_2CHX$	0.55	8.0	4
Polysubstituted ethanes	..	..	10, 11
$\begin{array}{c} H_A \\ \diagdown \\ C=C \\ \diagup \\ H_B \end{array} \begin{array}{c} X \\ \diagdown \\ C=C \\ \diagup \\ H_C \end{array}$	$J_{BC}$ (cis) 4.2	24.5	8 (cf. 5-7)
	$J_{AC}$ (trans) 3.5	27.3	8 (cf. 5-7)
Polysubstituted cyclopropanes	$J$ (cis) 2.8	13.6	
	$J$ (trans) 2.4	17.7	9, 12a
II	$J_{BX}$ (cis) 1.4	12.6	12
	$J_{AX}$ (trans) 1.7	8.8	12
I	$J_{ef}$ (cis) 1.0	11.3	This study

<sup>a</sup> Estimated from the equation<sup>4</sup>  $J_{obad} = J_0 - \alpha E_R$ , using the slopes of the published curves in the references cited.

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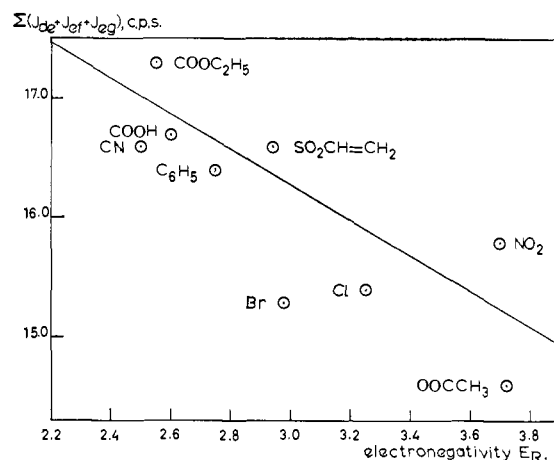


Fig. 4.—Variation of the sum of coupling constants  $\Sigma(J_{de} + J_{ef} + J_{eg})$  with the electronegativity of substituents.

are summarized in Table IV. Smaller substituent effects on the other coupling constants reported in Table II also appear to be present, but their significance is difficult to assess.

Our data (Fig. 2 and 3) and similar plots in the literature show considerable scatter. This is not surprising because of steric and other effects of substituents. What is noteworthy is that electronegativity of substituents definitely influences coupling constants. The magnitude of this effect (measured by  $\alpha$  in Table IV) is most pronounced in olefinic systems, intermediate in the bicyclic examples studied, and smallest in the simple acyclic cases. This suggests, perhaps, that a substantial amount of  $\pi$ -electron delocalization exists in the bicyclic systems due to strain, as postulated by Musher for norbornane derivatives.<sup>18</sup> Changes in azimuthal angle do not seem to have a marked influence on  $\alpha$ .

These results emphasize the dangers inherent in uncritical application of the Karplus curve to calculation of azimuthal angles in organic molecules. Electronegativity effects with substituents often encountered can be as high as 20% of the measured coupling constants for saturated compounds and considerably higher for unsaturated systems. Furthermore, the magnitudes of vicinal  $J$ 's are also dependent on other factors. *cis*-Olefinic coupling constants vary markedly with ring size.<sup>19</sup> It also appears for the present study that  $J$  is not, as has been suggested,<sup>12,20</sup> independent of carbon hybridization. For norbornene derivatives (Table II) differences are observed in the same molecules with rings of the same sizes when  $\phi = 0$ ; the olefinic coupling constants  $J_{bc}$  ranged from 5.3 to 5.8 c.p.s. while the aliphatic constants  $J_{ef}$  varied from 7.8 to 9.2 c.p.s.

## Experimental

A Varian A-60 n.m.r. spectrometer was used to determine the spectra. Samples were run as 10% solutions in  $CCl_4$  with tetramethylsilane internal reference at the operating temperature of the instrument (*ca.* 35°). The instrument sweep was calibrated with chloroform and the peak positions read from the spectra; chemical shifts are probably accurate to  $\pm 1$  c.p.s. and coupling constants to  $\pm 0.1$  c.p.s. The samples were well known Diels-Alder adducts of monosubstituted ethylenes and cyclopentadiene. Preparative gas chromatography was used in some cases to separate the predominant *endo* isomers I from the adduct mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL]

## The Formation of Solvated Electrons in the Photochemistry of the Phenolate Ion in Aqueous Solutions

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Evidence for the photochemical formation of solvated electrons in aqueous solutions of the phenolate ion is obtained.  $N_2O$  and acetone are employed as specific scavengers for the solvated electrons produced from the thermal dissociation of the excited state. The dependence of the quantum yield of  $N_2$  on  $[N_2O]$  is found to agree with cage scavenging kinetics. The solvated electron–phenoxyl radical pair in the solvent cage is formed in a secondary process from the spectroscopic excited state of the ion. Spectroscopic data indicate that this excited state arises from an internal  $\pi-\pi^*$  excitation and does not involve a c.t.t.s. (charge transfer to the solvent) state as in the case of solvated electron formation in the photochemistry of the halide ions in solution.

### Introduction

The occurrence of photoionization processes of aromatic molecules in rigid solvents was first established by the pioneering work of Lewis and his school.<sup>1,2</sup> Later investigators<sup>3,4</sup> considered the nature of the photoejected electron, trapped by solvation in the rigid glass, and followed the kinetics of the electron–radical ion recombination luminescence. Land, Porter, and Strachan<sup>5</sup> were able to prove that such photoionization processes are not restricted to condensed glassy media and may also occur in liquid solutions. This was accomplished by comparing the spectra of the short-lived intermediates formed in the flash photolysis of a large number of phenols and naphthols in water<sup>5</sup> with the photolysis products obtained from the same molecules in rigid solution.<sup>6</sup> It was thus suggested<sup>5,7</sup> that the primary photochemical act in the case of aqueous phenolate ion involves an electron ejection process. These conclusions were recently confirmed by an investigation<sup>8</sup> of the photochemistry of the phenolate ion in aqueous and alcoholic NaOH–KOH glasses at 77°K. where the spectrum of the trapped, photoejected, electron was identified.

The purpose of the present work was to provide direct chemical evidence for the photoionization of the phenolate ion in aqueous solutions, to get a closer insight into the electron ejection process, and to investigate the fate of the ejected electron in this system. In previous work<sup>9–11</sup> we investigated the photochemical consequences of light absorption in the charge transfer to the solvent (c.t.t.s.) bands of the monoatomic negative halide ions in solution. By using specific scavengers, chemical evidence was obtained here for the transient formation of solvated electrons by thermal ionization of the c.t.t.s. excited state. These chemical kinetic methods, in which specific scavengers for solvated electrons are employed, were now applied to the investigation of the photochemistry of the phenolate ion, providing us with new tools in the study of photoionization processes of molecules in solution.

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### Experimental

**Light Sources and Actinometry.**—The light source at 229  $m\mu$  was an Osram Cd/1 cadmium lamp operated at 12 v. and 1.5 amp. The spectral distribution of the lamp was determined by an Optica CFU spectrophotometer. The only lines absorbed by our solutions were the 2288 Å. line and the very weak 2144 Å. line. The light output at 2288 Å. was determined by a differential actinometric method using the uranyl oxalate actinometer. In a first experiment the actinometric solution in the reaction vessel was irradiated directly. In a second experiment a 1-cm. path length 4 *N* acetic acid solution filter, absorbing all the light below 2400 Å., was inserted between the reaction vessel and the lamp. The chemical change on illumination was determined in both cases by titration with 0.01 *N*  $KMnO_4$  solution. From the difference between the two values the light intensity at 2288 Å. was determined as  $J = 3.4 \times 10^{-7}$  einstein  $l^{-1} \text{ sec}^{-1}$ .

The light source at 2537 Å. was a Thermal Syndicate low pressure mercury arc operated at 1000 v. and 50 amp. A  $I_2/I^-$  filter<sup>9</sup> was employed to cut off other lines. The light intensity at this wave length was  $J = 8.1 \times 10^{-7}$  einstein  $l^{-1} \text{ sec}^{-1}$ .

**Procedure.**—A 1-cm. quartz spectrophotometer cell was adapted for vacuum-photochemical experiments.

The procedure in experiments involving  $N_2O$  was previously described.<sup>10</sup> The pressure of the gas evolved after irradiation was determined by means of a McLeod gage and its composition ascertained by combustion in the presence of hydrogen or oxygen. The pH was adjusted by means of NaOH.

In all cases total light absorption by the phenolate ion in the reaction cell could be assumed (see Fig. 4 for the values of the extinction coefficients). Absorption of light by the  $OH^-$  ion could be neglected even at 2288 Å. as here  $\epsilon_{OH^-} = 0.5 \text{ l. mole}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{C_6H_5O^-} = 7500 \text{ l. mole}^{-1} \text{ cm}^{-1}$ , and  $[C_6H_5O^-]/[OH^-]$  was never below 0.1. The same refers to absorption of the 2144 Å. cadmium line, which is approximately one-thirtieth that of the 2288 Å. line (here  $\epsilon_{OH^-} = 15 \text{ l. mole}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{C_6H_5O^-} = 4000 \text{ l. mole}^{-1} \text{ cm}^{-1}$ ).

### Results and Discussion

**The Phenolate– $N_2O$  System.**—Experiments were carried out with aqueous solutions of  $10^{-3} M$  phenol,  $10^{-2} M$  NaOH, 1 *M* ethanol, and varying concentrations of dissolved  $N_2O$ . At pH 12 almost all the phenol ( $pK_a = 10$ ) exists in its ionized form. Ethanol was added in order to scavenge  $OH$  (or  $O^-$ ) radicals, thus preventing the formation of  $H_2O_2$  which may cause, by further reactions with  $OH$  radicals, the evolution of  $O_2$  as a second gaseous product. The gas evolved on irradiating the solutions was found to be pure  $N_2$ . From the slopes of the linear plots of  $[N_2]$  vs. the irradiation time, we calculate the quantum yields for  $N_2$  evolution,  $\gamma(N_2)$ , which depend markedly on the  $N_2O$  concentration. These results are presented in Table I.

An examination of Table I shows that the ratio  $\gamma(N_2)_{2288 \text{ Å.}}/\gamma(N_2)_{2537 \text{ Å.}}$  is constant at constant  $N_2O$  concentration. At high  $[N_2O]$  values a limiting constant quantum yield independent of  $[N_2O]$  is obtained.