the findings regarding the effect of substituent on the chemical shifts of adjacent protons until more compounds have been examined.

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# Nuclear Magnetic Resonance Study of Acetyl Exchange between Acetic Acid and Acetic Anhydride

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The exchange rate of acetyl groups between acetic acid and acetic anhydride was measured using the nuclear magnetic resonance techniques. The exchange is strongly acid catalyzed. The rate of exchange was measured at $22 \pm 1°$ as a function of $AcOH$, $Ac_2O$, and $HClO_4$ concentrations using $CHCl_3$ as a diluent. It was found that the exchange rate is proportional to $HClO_4$ concentration, increases with $Ac_2O$ concentration, and for concentrated solutions of $AcOH$ and dilute $Ac_2O$ is independent of $AcOH$ concentration. The experimental results are discussed in terms of four possible exchange mechanisms. Kinetically it is shown that the perchloric acid predominantly protonates acetic acid molecules. Over a limited concentration range where the exchange rate is independent of $AcOH$ concentration, the results can be explained as a bimolecular reaction between a protonated acetic acid molecule $(AcOH_2{}^+)$ and a neutral acetic anhydride molecule with a rate constant $k = 560 \ sec.^{-1} \ M^{-1}$. Outside this range no simple mechanism seems to fit the experimental results.

## Introduction

The occurrence of exchange reactions of the acetyl group between aliphatic acids and anhydrides is well known. Evans, Huston, and Norris[1] have studied the exchange reaction in neutral acetic acid–acetic anhydride system, using the carbon labeling technique. They found that the half-life time of the exchange of acetic anhydride in solvent acetic acid is approximately 10 hr. while that of acetic acid in solvent anhydride is 5 hr.

The exchange reaction between acetic acid and acetic anhydride is strongly acid catalyzed and at appreciable acid concentrations becomes so fast that its investigation by isotope labeling techniques becomes impossible. In the work reported here the nuclear magnetic resonance (n.m.r.) technique, which was previously applied to the study of hydrogen exchange,[2] was used for the investigation of the acetyl group exchange in this system.

The exchange rate was measured as a function of the concentration of perchloric acid, of acetic acid, and of acetic anhydride.

The acetic acid–acetic anhydride system is important as an acetylating agent. The acetylation reaction is catalyzed by perchloric acid. The kinetics of this reaction is discussed by Mackenzie and Winter,[3] and by Burton and Praill.[4] These authors assumed that the exchange of an acetyl group between acetic acid and acetic anhydride, which results in the formation of an $Ac^+$ ion, is the first step in the acetylation reaction.

## Experimental

The main features of the n.m.r. spectrometer have been described previously.[5] The proton frequency was 31.6 Mc.p.s. The sample holders used were cylindrical glass tubes of about 3-mm. d. They were rotated by a small air turbine. The field homogeneity was such that an effective $T_2$ in water of about 1.2 sec. was observed from the decay of the "wiggles" on fast passage.

*Reagents and Preparation of Solutions.* B.D.H. acetic acid and chloroform A.R. were used without further purification. The acetic anhydride was Baker and Adamson, ACS grade, and was distilled once. The perchloric acid was 70% A.R., supplied by Mallinckrodt. Its titer was determined by titration against NaOH, using methyl orange as the indicator.

To study the dependence of exchange rate on the concentration of the different species, solutions were prepared in series, the members of each series differing only in the concentration of a single component. The preparation procedure was as follows: for each such series two stock solutions, differing only in the concentration of one of the components, were prepared. By mixing known quantities of the two stock solutions, a series of varying concentration in the desired species was obtained, while the concentration of all the others remained constant. For example, for measuring the dependence of the rate of exchange with respect to

(1) E. A. Evans, J. L. Huston, and T. H. Norris, *J. Am. Chem. Soc.*, **74**, 4985 (1952).
(2) See, *e.g.*, A. Lowenstein and T. M. Connor, *Ber. Bunsenges. physik. Chem.*, **67**, 280 (1963).
(3) H. E. Mackenzie and E. R. S. Winter, *Trans. Faraday Soc.*, **44**, 159 (1948); **44**, 171 (1948); **44**, 243 (1948).
(4) H. Burton and P. E. G. Praill, *J. Chem. Soc.*, 1203, 2034 (1950); 226, 522, 529 (1951).
(5) E. Grunwald, A. Lowenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).
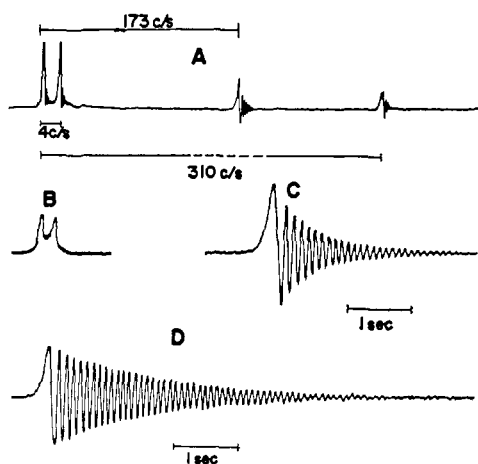
Figure 1. Typical n.m.r. spectra at 31.6 Mc./sec. of the studied solutions and the changes of the line shape due to different exchange rates. (A) N.m.r. spectrum of a neutral solution of acetic acid, acetic anhydride, and chloroform. The lines from left to right, in order of decreasing field, are due to: the methyl group of acetic acid, the methyl groups of acetic anhydride, the proton of the chloroform, and the proton of the carboxylic group of acetic acid. (B) The same solution after a small amount of $HClO_4$ was added. Only the broadened methyl lines of the two species are shown. (C) The resonance of the methyl protons when the exchange is fast. A single line is observed for both species. The line is recorded using fast passage. (D) The line of the proton of the carboxylic group recorded at fast passage.

perchloric acid concentration, both stock solutions contained identical concentrations of acetic anhydride and of acetic acid, while one of them contained also perchloric acid. In preparing the acidified stock solution the quantities of acetic acid and acetic anhydride to be used were calculated taking into account the conversion of acetic anhydride to acetic acid by the water in the perchloric acid.

**Determination of Rate Constants**

The n.m.r. spectrum of neutral solutions of acetic acid–acetic anhydride mixtures in chloroform consists of four sharp lines (Figure 1A). In order of decreasing field, these lines are (1) the proton resonance of the acetic acid methyl group, (2) the proton resonance of the anhydride methyl group, (3) the proton resonance of the chloroform protons, and (4) the proton resonance of the acetic acid carboxyl group. On acidification (by the addition of perchloric acid) the exchange rate increases. This results in the broadening of the methyl resonances and, at still higher exchange rates, in their collapse into a single line (Figures 1B and 1C). From a quantitative measurement of the observed line widths, the rate of exchange can be calculated.

We studied the system when the exchange was so fast that the methyl group resonances of acetic anhydride and acetic acid collapsed into a single peak. The width of this peak was determined from the decay time of the "wiggles" ($T_2$) following fast passage. Each measurement was repeated four to five times and the average value was used. The scatter of the experimental points was within 10%.

Under these conditions the rate of exchange between the two species is related to the observed line width by eq. 1,[6] where $T_2$ is the observed line-width parameter,

(6) S. Meiboom, Z. Luz, and D. Gill, *J. Chem. Phys.*, 27, 144 (1957).

$$\frac{1}{T_2} = \frac{1}{T_2'} + (\delta\omega)^2 P_A^2 (1 - P_A)^2 (\tau_A + \tau_B) \qquad (1)$$

$T_2'$ is the line-width parameter in the absence of exchange, $\delta\omega$ is the chemical shift between the exchanging groups in radians per second, $P_A$ is the methyl proton fraction of component A (either acetic acid or acetic anhydride), $\tau_A$ is the average lifetime of component A between successive exchanges, and $\tau_B$ is the average lifetime of the second component. Equation 1 applies if

$$\delta\omega << \left(\frac{1}{\tau_A} + \frac{1}{\tau_B}\right)$$

Obviously

$$P_A\tau_B = (1 - P_A)\tau_A$$

The above condition was fulfilled in our measurements. For each composition of the solutions $\delta\omega$ was measured directly in an unacidified solution using the side-band technique.

The line-width parameter in the absence of exchange, $T_2'$, can in principle be obtained from line-width measurements in neutral samples (in which the exchange is so slow that its contribution to the line width can be neglected). However, an appreciable part of the observed line width is caused by inhomogeneity broadening, and the latter is liable to vary with time and upon changing the sample. In order to avoid errors which such variations would involve, the $T_2$ of the carboxylic hydrogen was determined in each sample, and this value was assumed to be representative for the $T_2$ of the methyl resonances in the same sample. Though the methyl and carboxyl peaks cannot be expected to have exactly the same natural line width, the latter contributes only a small correction in eq. 1, and an error in its estimate is hardly of consequence.

The average lifetime between exchanges of a component A, ($\tau_A$), is related to the rate of exchange of A, $d[A]/dt$, by eq. 2.

$$\frac{1}{\tau_A} = \frac{1}{[A]} \frac{d[A]}{dt} \qquad (2)$$

In what follows, A will denote acetic acid.

**Experimental Results**

The exchange reaction is strongly acid catalyzed. Experimental results on acetic acid–acetic anhydride mixtures are summarized in Figure 2. In this figure, $1/\tau_A$ is given as a function of perchloric acid concentration for mixtures with different molar ratios of acetic anhydride to acetic acid. This figure shows that the rate of exchange varies linearly with $HClO_4$ concentration and increases with the mole fraction of acetic anhydride.

In order to reduce medium effects resulting from changing the composition of the mixtures, each of the solutions studied was diluted to twice its volume with chloroform, and the spectra were rerun. Results of these measurements have the same features as those shown in Figure 2. The only difference is in the numerical values of the slopes $1/\tau_A[HClO_4]$. These results are summarized in Table I.

After establishing the linear relation between $1/\tau_A$ and perchloric acid concentration, a more detailed
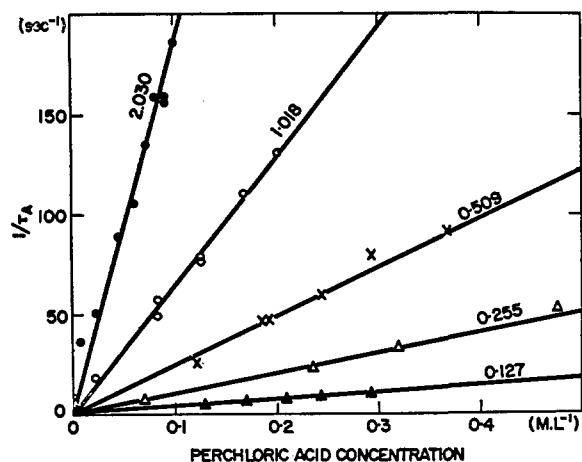
Figure 2. Values of $1/\tau_A$, the reciprocal of the mean lifetime between exchanges of the acetyl group of acetic acid, for various mixtures of AcOH and $Ac_2O$ as a function of [$HClO_4$]. The numbers above the curves represent the mole ratio [$Ac_2O$]/[AcOH] ($T = 22 \pm 1°$).



Figure 3. The rate of exchange of acetic acid per mole of $HClO_4$ ($T = 22 \pm 1°$), $1/[HClO_4] \times d[AcOH]/dt = [AcOH]/[HClO_4] \times 1/\tau_A$ for various acetic anhydride concentrations as a function of acetic acid. (The mixtures were diluted with chloroform). The concentrations of $Ac_2O$ and $HClO_4$ (in parentheses) for each of the measured solutions were: $0.837$ $M$ ($0.165$ $M$), $1.26$ $M$ ($0.118$ $M$), $3.79$ $M$ ($0.095$ $M$ and $0.047$ $M$ for [AcOH] $> 4$ $M$), $4.027$ $M$ ($0.078$ $M$), respectively. Note the wide range for which the exchange rate is independent of [AcOH] for low [$Ac_2O$].

study of the dependence of the exchange rate on the concentration of acetic acid and acetic anhydride was carried out. To do this we prepared sets of solutions in chloroform in which the acetic anhydride and perchloric acid concentrations were kept constant[7] and only the acetic acid concentration was varied. This was done for several concentrations of acetic anhydride. The rate of exchange of acetic acid per mole of perchloric acid, $(1/[HClO_4])d[AcOH]/dt = [AcOH]/\tau_A[HClO_4]$, found in these measurements are shown in Figure 3 as a function of acetic acid concentration. This figure shows that for low acetic anhydride concentration the rate of exchange (i.e., the number of acetyl groups exchanged between the two species) is independent of acetic acid concentration over a wide range of acetic acid concentrations, and depends only on the acetic anhydride concentration. However, for more concentrated acetic anhydride or dilute acetic acid solutions the rate of exchange increases with the decrease of acetic acid concentration.

In alkaline solutions, obtained by adding sodium acetate to acetic acid–acetic anhydride mixtures, the exchange was found to be too slow to be detected by broadening of the resonance lines. A mixture of about 0.2 mole fraction acetic anhydride and containing 0.3 $M$ sodium acetate did not show a detectable broadening

(7) The perchloric acid concentrations were chosen so that the exchange rate could be measured conveniently.
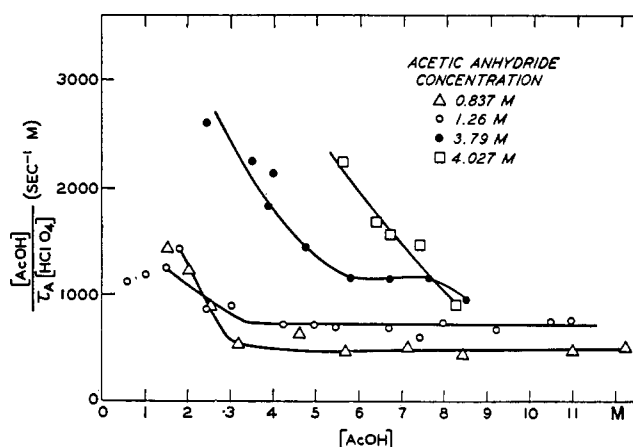
Table I. Values of $1/\tau_A[HClO_4]^a$

| [$Ac_2O$]/[AcOH] | A | | B | |
| | [AcOH] | $1/\tau_A \cdot$ [$HClO_4$], sec.$^{-1}$ $M^{-1}$ | [AcOH] | $1/\tau_A \cdot$ [$HClO_4$], sec.$^{-1}$ $M^{-1}$ |
| --- | --- | --- | --- | --- |
| 0.127 | 14.40 | 36 | 7.20 | 71 |
| 0.255 | 12.30 | 104 | 6.15 | 145 |
| 0.509 | 9.49 | 245 | 4.75 | 305 |
| 1.018 | 6.52 | 660 | 3.26 | 830 |
| 2.030 | 4.07 | 1865 | 2.04 | 2031 |

$^a$ For various mixtures of acetic anhydride and acetic acid (A) and solutions of these mixtures in equal volumes of chloroform (B).

of the methyl lines. From this observation it can be concluded that any exchange which may take place in this solution is associated with a mean lifetime longer than 2 sec.

The exchange of acetyl groups between acetic acid and methyl acetate was also studied. The n.m.r. spectra of two mixtures were examined. One mixture contained methyl acetate and acidified ($HClO_4$) acetic acid and the second contained methyl acetate, acidified acetic acid, and acetic anhydride. No exchange was observed in the first mixture, while for the second mixture, the exchange occurred only between acetic acid and acetic anhydride. This result indicates that the mean lifetime of the acetyl group of methyl acetate is longer than 2 sec.

Before proceeding with the discussion of the exchange mechanism it is necessary, at this stage, to mention some of the properties of the solutions investigated. Changing the composition of the solution results in a change in the dielectric constant (Table II) which may affect the rate of exchange. One might try to overcome this difficulty by working in dilute solutions. However, this would raise another problem. The monomer–dimer equilibrium of acetic acid changes with dilution, which again may influence the rate of exchange.[8,9]

Since the dielectric constant of most of the measured solutions is low, each of the three ionic species exist in two forms, the free ion and the ion pair. The question which arises is which of the two ionic forms takes part in the exchange reaction. If the free ion participates in the exchange, it is expected that an increase of the dielectric constant, which results in the increase of the dissociation of the ion pair, will increase the rate of

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 415.
(9) Our measurements show that, even in the region we have studied, the chemical shifts of the protons of the carboxylic group changed toward higher field as referred to the line of the methyl group when the concentration of AcOH was less than 2 $M$. This probably indicates a shift in the monomer–dimer equilibrium.

**Table II.** The Dielectric Constants[a]

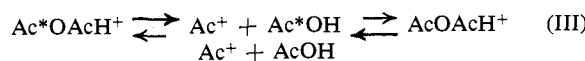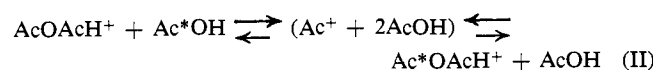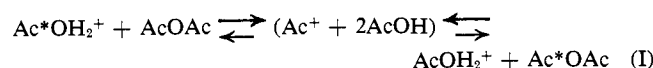| [Ac₂O]/[AcOH] | Dielectric constant | |
|---|---|---|
| | A | B |
| 2.030 | 17.0 | 11.7 |
| 1.018 | 14.9 | 10.0 |
| 0.509 | 12.5 | 9.1 |
| 0.255 | 10.4 | 7.7 |
| 0.127 | 8.9 | 6.5 |

[a] For various mixtures of acetic anhydride–acetic acid (A) and for solutions of these mixtures in equal volumes of chloroform (B).

exchange. In principle this question could be solved using conductivity measurements. Such measurements were not done. However, the fact that the rate of exchange depends linearly on $HClO_4$ concentration for each ratio of AcOH to Ac₂O indicates that the free ion is not responsible for the exchange since otherwise it is expected that association of the free ions would occur with the increase of $[HClO_4]$,[10] and the rate should deviate from linearity. In the following discussion we will disregard the problem of ion pairs.

## Discussion

*(1) Kinetic Mechanisms.* It is known that in the presence of acetic acid the perchloric acid is completely ionized and forms ion pairs, the dissociation of which is very small.[11,12] It is probable that in the mixture of acetic acid and acetic anhydride the perchloric acid is also completely ionized. In this case the perchloric acid can protonate either the acetic acid, or the acetic anhydride, or both. Thus the following ionic species may exist in the solution: $AcOH_2^+$, $Ac_2OH^+$, and $Ac^+$ (see later discussions). As the observed rate of exchange is first order with respect to hydrogen ion concentration it is obvious that the reaction involves one of these ions.

The exchange of an acetyl group between acetic acid and acetic anhydride can be described by mechanisms I–III, where the quantities in parentheses describe the

$$Ac^*OH_2^+ + AcOAc \rightleftarrows (Ac^+ + 2AcOH) \longrightarrow$$
$$AcOH_2^+ + Ac^*OAc \quad (I)$$

$$AcOAcH^+ + Ac^*OH \rightleftarrows (Ac^+ + 2AcOH) \longleftarrow$$
$$Ac^*OAcH^+ + AcOH \quad (II)$$

$$Ac^*OAcH^+ \rightleftarrows Ac^+ + Ac^*OH \rightleftarrows AcOAcH^+ \quad (III)$$
$$Ac^+ + AcOH$$

intermediate species in the chemical reaction, and the longer arrows describe the slowest (rate-determining) step in the reactions.

Reactions I and II are bimolecular reactions, a protonated and a neutral molecule react forming the species in brackets which can then react in different ways leading to the exchange of the starred acetyl group (Ac*).

In reaction III the rate-determining step is the monomolecular dissociation of the $Ac_2OH^+$ ion into an $Ac^+$ ion and acetic acid. The $Ac^+$ formed in this way reacts with an AcOH molecule different from that formed in the dissociation.

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p. 72.
(11) I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1007 (1934).
(12) I. M. Kolthoff and S. Bruchenstein, *ibid.*, **78**, 1 (1956).

Another possibility which has to be considered (denoted as mechanism IV) is that the acetyl ion ($Ac^+$) is the predominant ion in the solution. In this case the exchange rate will be dominated by the reaction described by the shorter arrows in eq. I–III. All these are reactions between an ion and acetic acid and therefore kinetically equivalent to reaction II.

At this stage we treat the $Ac^+$ ion as a well-defined entity. There is of course no real evidence for the existence of such an ion which presumably reacts strongly with the medium. The same kinetic results for mechanisms I and II would be obtained if one replaced the species in brackets in the equations by some sort of activated complex which can break up in different ways so as to give exchange.

*(2) Comparison with Experiments.* The behavior of the system is quite complicated and it is not possible to untangle the different reaction mechanisms without simplifying assumptions.

The simplest assumption would be that there is essentially one ionic species in the solution which is responsible for the exchange, and whose concentration equals the concentration of perchloric acid added. One then has eq. 3–5 for the four reactions con-

$$\frac{1}{[HClO_4]} \frac{d[AcOH]}{dt} = k_I[Ac_2O] \quad (3)$$

$$\frac{1}{[HClO_4]} \frac{d[AcOH]}{dt} = k_{II}[AcOH] \text{ or } k_{IV}[AcOH] \quad (4)$$

$$\frac{1}{[HClO_4]} \frac{d[AcOH]}{dt} = k_{III} \quad (5)$$

sidered.[13]

For low acetic anhydride and high acetic acid concentration it is then possible to fit the experimental results by mechanism I (see Figure 3). This would imply that the protonation occurs predominantly on acetic acid. None of the other mechanisms fits the experimental results at all. In a way the solutions in which this mechanism works can be regarded as dilute solution of acetic anhydride in acetic acid, *i.e.*, as dilute solutions in the usual sense. The deviations at high anhydride concentrations can be attributed to changes in the medium.

The conclusion that protonation occurs mainly on acetic acid is corroborated by other experiments on these systems.[14,15] It was found in these experiments that in a solvent of low basic strength, such as acetic anhydride, amides and polypeptides can be titrated as bases by $HClO_4$. Even small amounts of acetic acid in these solutions interfere with the titration and the end point is smeared out. The acetic acid therefore competes with the amide group in binding protons whereas the solvent acetic anhydride does not. One may conclude that acetic acid is by far more basic than acetic anhydride, and will be protonated more easily.

From eq. 3 and the experimental data one can calculate that $k_I = 560$ sec.$^{-1} M^{-1}$, which describes the

(13) It should be noted that the rate constants $k_I, k_{II}$, and $k_{III}$ above are effective constants for the exchange reaction observed. They are proportional to the rate constants of the heavy arrows in eq. I–III but not necessarily equal to them. The relation between the two sets of constants depends on the exact nature of the bracketed state, which is not known.
(14) D. C. Wimer, *Anal. Chem.*, **30**, 77 (1958).
(15) I. Z. Steinberg, W. F. Harrington, A. Berger, M. Sela, and E. Katchalski, *J. Am. Chem. Soc.*, **82**, 5263 (1960).

observed exchange rate for low [Ac$_2$O] and high [AcOH] (Figure 3).

One now has to consider the possibility that the rate constants are such that the exchange is not determined by the most abundant ion. It can be seen from the kinetic equations that reaction IV cannot be important (*i.e.*, rate determining) unless the abundant ion is Ac$^+$. This reaction can thus be ruled out. We can then restrict ourselves to the consideration of the two ionic species AcOH$_2$$^+$ and Ac$_2$OH$^+$.

Considering the equilibrium between AcOH$_2$$^+$ and Ac$_2$OH$^+$ due to proton transfer and neglecting the concentration of Ac$^+$ one finds eq. 6 and 7, where $K$ is an equilibrium constant.
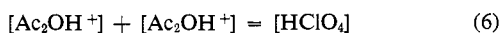
$$[Ac_2OH^+] + [Ac_2OH^+] = [HClO_4] \tag{6}$$

and

$$K = \frac{[Ac_2OH^+][AcOH]}{[AcOH_2^+][Ac_2O]} \tag{7}$$

If we assume that $K$ does not change with composition, the rate of exchange for mechanisms I–III is then given by eq. 8–10.

$$\frac{1}{[HClO_4]}\frac{d[AcOH]}{dt} = k_I\frac{[Ac_2O][AcOH]}{[AcOH] + K[Ac_2O]} \tag{8}$$

$$\frac{1}{[HClO_4]}\frac{d[AcOH]}{dt} = k_{II}\frac{K[Ac_2O][AcOH]}{[AcOH] + K[Ac_2O]} \tag{9}$$

$$\frac{1}{[HClO_4]}\frac{d[AcOH]}{dt} = k_{III}\frac{K[Ac_2O]}{[AcOH] + K[Ac_2O]} \tag{10}$$

Equations 8 and 9 show that reactions I and II differ only by a constant $K$ and are therefore kinetically indistinguishable.

As discussed earlier, the observed exchange rate is linear in [Ac$_2$O] and independent of [AcOH] for relatively high [AcOH] and low [Ac$_2$O]. This can be fitted both by eq. 8 (mechanism I) and 9 (mechanism II) if $K << 1$, so that [AcOH] $>> K$[Ac$_2$O].

If mechanism II is important we require $Kk_{II} \approx 560$ sec.$^{-1}$ $M^{-1}$, as is immediately obvious from our previously quoted value of $k_I$ and a comparison of eq. 8 and 9. Since $K << 1$ this requires a very large rate constant $k_{II}$ which does not seem reasonable for a reaction of this type.

According to mechanism III the rate of exchange should be proportional to acetic anhydride concentration and to the reciprocal of acetic acid concentration. This seems to agree qualitatively with the results at low acetic acid and high acetic anhydride concentration. However, attempts to fit numerically the rates calculated according to mechanism III with the experimental results failed.

*Acknowledgment.* This work was started in collaboration with Professor S. Meiboom. We would like to express our gratitude for his large contribution to this work and for important comments on the manuscript. We also wish to thank Dr. D. Gill and M. Sasson who designed and built the bridge for measuring dielectric constants and to Professor E. Grünwald for helpful discussion.

# Electron Paramagnetic Resonance Spectra of Semiquinones. II. Coupling Constants of β-Nuclei[1]

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*The electron paramagnetic resonance spectra of 2-t-butyl-, 2-t-butyl-C$^{13}$-, and 2-trifluoromethylsemiquinone and the semiquinones prepared from 1-methyl-2,5-dihydroxy- and 2,5-dihydroxytriptycene were obtained. Coupling constants for β-C$^{13}$ and β-F are 0.74 and 2.66 gauss, respectively. The bridgehead hydrogen atoms of the triptycene derivatives are not coupled. The results are discussed with reference to the conclusions of reaction chemistry concerning the relative importance of C–H, C–C, and C–F hyperconjugation.*

## Introduction

Electron paramagnetic resonance spectra offer a method for the determination of spin density at the nuclei of complex free radicals.[2,3] In brief, radicals

of structure I (X = H) have large spin density at the nonbonded atom. Early theoretical treatments stressed

I
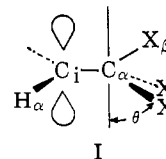
the significance of C–H hyperconjugation.[4,5] McLachlan suggested spin polarization as an alternative.[6] Strauss and Fraenkel subsequently found that the spin-polarization model overestimated the spin density at the $\alpha$-carbon atom.[7] Other work revealed that the spin density at nonbonded hydrogen atoms is greater for positive-ion radicals than for negative-ion radi-

(2) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 183 (1963).
(3) A. Carrington, *Quart. Rev.* (London), **17**, 67 (1963).
(4) R. Bersohn, *J. Chem. Phys.*, **24**, 1066 (1956).
(5) D. B. Chestnut, *ibid.*, **29**, 43 (1958).
(6) A. D. McLachlan, *Mol. Phys.*, **1**, 234 (1958).
(7) H. L. Strauss and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1768 (1961).