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Studies of the Rate of Acid Catalysed Oxygen Exchange between Ketones and ^{18}O-Enriched Water in Acetonitrile by Infrared Absorption Analysis

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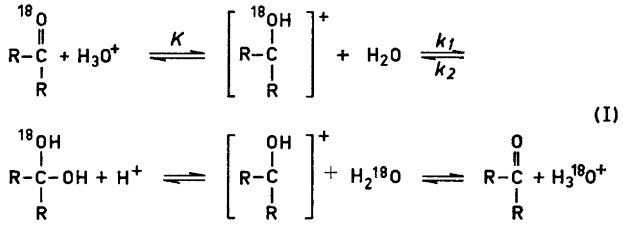
The paper reports kinetic studies of the acid catalysed oxygen exchange between ^{18}O-enriched water and acetone, acetophenone, and benzophenone in acetonitrile. The reaction has been followed by measuring the optical density of the $C=^{18}O$-stretching band in infrared. It is concluded that protonation of the ketones cannot be the rate determining step of the exchange process.

Rate studies of the oxygen exchange between ketones and water are rather scanty. The field has lately been reviewed by Samuel and Silver.[1] The classic study of oxygen exchange in carbonyl compounds is due to Cohn and Urey [2] who found that acetone as well as acetaldehyde exchange oxygen with water, the latter more rapidly. In the case of acetone, general acid, but not general base catalysis was observed. Menon [3] has measured the rate of acid and base catalysed oxygen exchange between *p*-substituted benzophenones and water in 80 % dioxane-water. For the acid catalysed reaction the following mechanism was suggested:



(I)

k_1 is assumed to be the rate determining constant for the reaction. The lack of marked differences in relative rates of exchange of different *p*-substituted benzophenones was attributed to opposing effects on the equilibrium constant K and the rate constant k_1 in the rate scheme.

Besides the two rate studies mentioned above, some semiquantitative studies of oxygen exchange in ketones have been reported.[4] The fact that so few studies are reported in this field is most likely due to the expensive experimental requirements, since mass spectroscopic analysis has been the usual method for determination of the isotope content of reactant or product. Pinchas *et al.*[5,6] showed that several infrared bands which are due to stretching between oxygen and other atoms (P,S,C) are often sufficiently displaced by change of isotopic oxygen from ^{16}O to ^{18}O to obtain quantitative resolution of the bands. Such a method was used by us [7] in a previous study to measure the isotope content in the P=O group in dialkyl phosphonates. The promising results stimulated the present study in which the infrared method has been used to measure the ^{18}O-content in the ketones during oxygen exchange between ^{18}O-enriched water and ketones in acetonitrile.

EXPERIMENTAL

Materials. Acetone and *acetophenone* were fractionated before use until their gas chromatographic spectra showed less than 1 % of impurities.

Benzophenone was recrystallized two times from alcohol, m.p. 51.5–52.5°C.

Acetonitrile was thoroughly dried by boiling with phosphorus pentoxide for 1 h. The fraction boiling between 81 and 81.5°C was used.

^{18}O-Enriched water, produced by Yeda Research and Development Co. Ltd., Rehovoth, Israel, had the following specifications: ^{18}O: 86.36 atom %, ^{17}O: 0.14 atom%.

Rate measurements. The measurements of the ^{18}O-exchange between the ketones and water were performed in dilute acetonitrile solution with ketone concentration in the range 0.075–0.1 M and $H_2{}^{18}O$-concentration in the range 0.07–0.18 M. The formation of ^{18}O-containing ketone was followed by measuring the optical density of the $C=^{18}O$ stretching vibration band in infrared directly in acetonitrile solution. The three ketones studied had the following $C=^{16}O$ and $C=^{18}O$ frequencies in acetonitrile: acetone, 1728 and 1695 cm^{-1}; acetophenone, 1700 and 1668 cm^{-1}; benzophenone, 1675 and 1646 cm^{-1} (Fig. 1). The infrared spectra were recorded on a high resolution Unicam S. P. 100, Mk 2-infrared instrument fitted with sodium chloride prism as well as grating optics. The samples were measured in 0.1 mm sodium chloride cells. In every run 10–20 measurements were taken.

Rate calculations. The rate of ^{18}O-exchange between ketones and $H_2{}^{18}O$ in acetonitrile is calculated according to the following eqn.:

$$\underset{(a-x)}{R_2C=^{16}O} + \underset{(b-x)}{H_2{}^{18}O} \underset{k^{16}}{\overset{k^{18}}{\rightleftharpoons}} \underset{(x)}{R_2C=^{18}O} + \underset{(c+x)}{H_2{}^{16}O} \qquad (1)$$

where a, b, and c are start concentrations of $R_2C=^{16}O$, $H_2{}^{18}O$ and $H_2{}^{16}O$, respectively, and x = concentration of $R_2C=^{18}O$ after the time t. k^{18} and k^{16} are the rate constants for the ^{18}O-respectively, ^{16}O-exchange. Eqn. (1) results in the following rat eqn.:

$$dx/dt = k^{18}\ (a-x)\ (b-x) - k^{16}\ x\ (c+x) \qquad (2)$$

If it is assumed that the rate of ^{18}O- and ^{16}O-exchange is equal, *i.e.* $k^{18} = k^{16}$, eqn. (2) reduces to a simple first order eqn.:

$$dx/dt = k^{18}\ [(a-x)\ (b-x) - x(x+c)] = k^{18}\ [ab-(a+b+c)x] \qquad (3)$$

Eqn. (3) has the solution:

$$k^{18}t = \frac{1}{a+b+c}\ \ln\left[\frac{ab}{a+b+c}\Big/\left(\frac{ab}{a+b+c} - x\right)\right] \qquad (4)$$

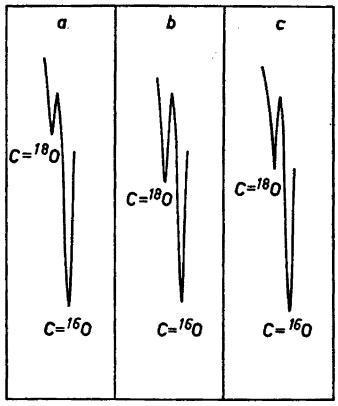


Fig. 1. Infrared stretching vibration bands of C=^{18}O and C=^{16}O of ketones in acetonitrile: a) acetone, b) acetophenone, c) benzophenone.

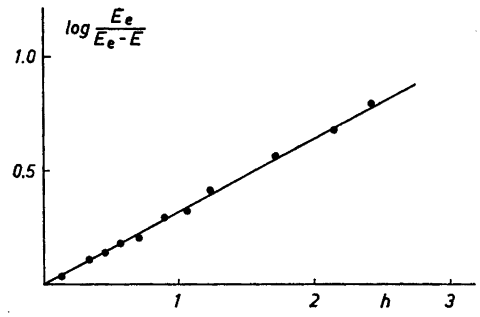


Fig. 2. First order plot for the acid catalysed oxygen exchange between acetone and 86.36 atom% ^{18}O-enriched water in acetonitrile. Acetone conc. 0.0744 M, $H_2{}^{18}O$: 0.1059 M. Temp. 30.2°C.

From eqn. (1) it is found that when $k^{18} = k^{16}$, the equilibrium concentration, $x_e = ab/(a + b + c)$, which introduced in eqn. (4) gives:

$$k^{18}t = \frac{1}{a + b + c} \ln \frac{x_e}{x_e - x} \tag{5}$$

When the optical density of the infrared C=^{18}O band, $E = \log T_0/T$, is introduced as relative measure of the concentration of $R_2C ={}^{18}O$, eqn. (5) is transformed to:

$$k^{18}t = \frac{2.303}{a + b + c} \cdot \log \frac{E_e}{E_e - E} \tag{6}$$

where E_e = optical density of C=^{18}O at equilibrium.

A typical kinetic run plotted according to eqn. (6) is shown in Fig. 2. Although the exchange has been followed to more than 90 % of completion, the experimental points lie still very near to a straight line expected for the first order plot. This observation thus confirms the correctness of assuming the rate of exchange of $H_2{}^{18}O$ and $H_2{}^{16}O$ with ketones to be alike, the postulate which forms the basis for the simplification of eqn. (2) to eqn. (3). The same result is also found earlier by Cohn and Urey.[2]

In Table 1 are recorded the specific rate constants for the exchange, obtained by dividing the first order rate constants with the concentration of hydrochloric acid.

RESULTS AND DISCUSSION

Rate data for the acid catalysed ^{18}O-exchange between $H_2{}^{18}O$ and three ketones are recorded in Table 1. The rate of exchange was found to be proportional to the hydrochloric acid concentration, in agreement with earlier observations for the exchange reaction in water [2] and in 80 % dioxan-water.[3]

The relative rates of oxygen exchange in benzophenone, acetophenone, and acetone are 1:60:1200. This great increase of rate makes a rate determining protonation of the ketones during exchange unlikely, since corresponding great differences in basicity of the ketones should then be expected. The following

Table 1. Rate data for the acid catalysed ^{18}O-exchange between ketones and $H_2{}^{18}O$ in acetonitrile. Content of ^{18}O in the water: 86.36 atom%.

Ketone	Temp. °C	HCl mole/l	Start conc. mole/l		Specific 2. order rate constant l/mole sec.
			Ketone	$H_2{}^{18}O$	
H_3C, CO, H_3C	30.2	1.2×10^{-5}	0.0751	0.08731	97.5
			0.0744	0.1059	87.4
Ph, CO, H_3C	30.2	2×10^{-3}	0.07834	0.0898	4.73×10^{-1}
			0.0669	0.0719	4.58×10^{-1}
Ph, CO, Ph	30.2	0.28	0.0995	0.1207	7.98×10^{-3}
		0.111	0.09368	0.07568	7.62×10^{-3}

small differences in pK_a-values for protonated ketones are found: [8] pK_a (acetone): -7.2, pK_a (acetophenone): -6.2, pK_a (benzophenone) $\approx$ pK_a (acetophenone).[9] Essentially the same result is reached on comparison of the association constants for the intermolecular hydrogen bonding between the same ketones and phenol in carbon tetrachloride:

$$\text{C=O} + \text{HOPh} \underset{}{\overset{K}{\rightleftharpoons}} \text{C=O}- - -\text{HOPh}$$

At 20°C the following values are found:[10] K (acetone): 12.3, K (acetophenone): 8.3, K (benzophenone): 7.8. The most plausible reaction mechanism for the acid catalysed exchange seems to be a rate determining reaction between a hydrogen bonded complex and $H_2{}^{18}O$ forming a tetravalent intermediate which rapidly breaks down:

$$R_2C={}^{16}O + H_3O^+ \rightleftharpoons R_2C={}^{16}O{-}{-}H_3O^+$$

$$R_2C={}^{16}O{-}{-}H_3O^+ + H_2{}^{18}O \rightleftharpoons \left[\begin{array}{c} H \\ {}^{18}O \\ H \end{array}\!\!\begin{array}{c} \\ \\ \end{array}\!\!\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\!\!=\!{}^{16}O\cdots H\!-\!O^+\!\!\begin{array}{c} H \\ \\ H \end{array}\right] \rightleftharpoons \quad \text{(II)}$$

$$\begin{array}{c} H \\ {}^{18}O^+ \\ H \end{array}\!\!\begin{array}{c} R \\ | \\ C \\ | \\ R \end{array}\!\!-{}^{16}OH + H_2{}^{16}O \rightleftharpoons R_2C={}^{18}O{-}{-}{-}H_3O^+ + H_2{}^{16}O$$

The reaction scheme (II) above differs from the scheme (I) suggested by Menon [3] in that no carbonium ion is formed by protonation of the ketone, instead a concerted mechanism is proposed in the second step. The mechanism is essentially the same as suggested by Bell *et al.* for the acid catalysed hydration of acetaldehyde.[11] The same general mechanism is also proposed by Jencks for the acid catalysed addition of nucleophiles to the carbonyl group.[12]

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