

Protonation of Acetone in Aqueous Mineral Acid Solutions

PENTTI SALOMAA and HANNU KEISALA

Department of Chemistry, University of Turku, Turku, Finland

The base strength of acetone has been discussed in several recent articles. The values given are, however, scattered over nearly seven pK units. For example, the following pK 's have been reported for the conjugate acid of acetone at 25°C: -1.44 (estimated from the influence of added acetone on the hydrolysis rate of ethyl acetate¹), -0.66 (calculated from the conductivity of acid solutions containing small amounts of acetone²), -7.2 (determined by indicator measurements in the ultra-violet³).

In connection with a kinetic study the activity coefficient of acetone was measured for a number of aqueous electrolyte solutions using the distribution technique. As the distribution of acetone between aqueous acids and an immiscible organic solvent has a close relation to the protonation equilibrium involved, the measurements were extended up to solutions of fairly high acidity.

The procedure used in the distribution measurements was the following. A measured volume (10 ml) of a standard acetone solution in chloroform (about 0.1 M) was mechanically stirred with an equal volume of the aqueous solution in an all-glass apparatus equipped with a thermostated jacket. After attainment of the distribution equilibrium, which took place in 10 to 16 h, the acetone concentration of the aqueous phase was determined by an improved iodoform method.⁴ The concentration of acetone in the organic phase was then calculated from the result of this analysis and from the initial concentration in chloroform. In a few cases the method was independently checked by determining the acetone remaining in the organic phase, whereupon conforming values were obtained. Care was taken to prevent any losses of acetone when neutralizing moderately acidic solutions by cooling the mixture below $+10^\circ\text{C}$ during the neutralization process.

Most of the results are shown in Fig. 1. The distribution coefficient K is defined by

$$K = [A]_{\text{org}}/[A]_{\text{aq}}$$

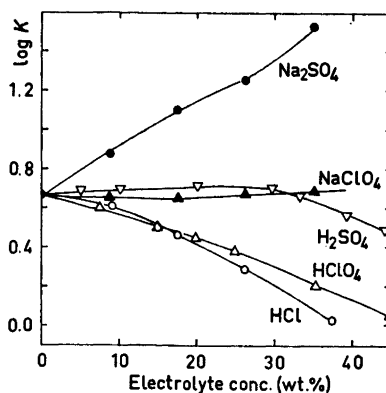


Fig. 1. Distribution of acetone between chloroform and aqueous electrolyte solutions at 25°C.

where the subscripts refer to chloroform and aqueous phases, respectively, and the concentrations are overall concentrations, irrespective of the molecular status of the solute in the phase in question. As the data for aqueous sulfuric acid solutions are of particular interest, these are given in detail in Table 1 over an extended acidity range. All values are averages of two to four determinations. The table also records values for the H_0 acidity function for the solutions used, as interpolated from the tables of Paul and Long.⁵

Fig. 1 indicates that there is a pronounced specificity in the electrolyte effects on the distribution equilibrium and hence on the activity coefficient of acetone in the aqueous phase. Similar behavior is also known from a number of other studies of activity coefficients of neutral molecules in electrolyte solutions.⁶ The shapes of the curves that relate to acid solutions indicate that in these solutions acetone is still remaining in its unprotonated form. If the protonation took place, one would expect the overall distribution coefficient K to begin to decrease more abruptly at a particular acid concentration, the curve assuming a shape similar to that of a titration curve, because the salt formed would be but slightly soluble in the organic phase in comparison to the unprotonated acetone. The pK value of -0.66 , derived from the conjugate acid of acetone from changes in conductivity,² would mean that acetone were half-protonated in about 15% sulfuric acid, in 16% perchloric acid and in

Table 1. Distribution coefficient of acetone between chloroform and aqueous sulfuric acid at 25°C.

% H ₂ SO ₄	H ₀	K
0	—	4.64
5.0	+0.11	4.85
10.0	-0.31	5.05
19.9	-1.00	5.20
29.7	-1.70	4.97
39.5	-2.37	3.65
44.3	-2.79	3.07
49.1	-3.28	2.18
53.8	-3.78	1.454
63.3	-4.84	0.836
68.1	-5.42	0.681
70.4	-5.70	0.626
72.7	-6.00	0.577
75.1	-6.31	0.507
77.4	-6.62	0.440
79.7	-6.93	0.371
82.0	-7.27	0.310
86.7	-7.87	0.229
91.2	-8.41	0.196
95.8	-8.88	0.187

7 % hydrochloric acid. It is seen from Fig. 1 that there is no exceptional activity behavior of acetone in this acidity range and therefore the protonation must occur at higher acidities.

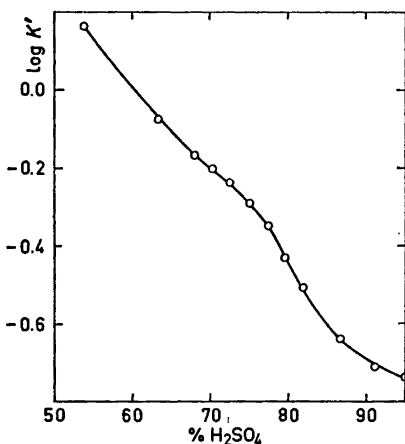


Fig. 2. Distribution of acetone between chloroform and moderately concentrated sulfuric acid solutions at 25°C.

Fig. 2, which illustrates the changes of the overall distribution coefficient K in relatively concentrated sulfuric acid solutions, reveals that above 70 % acid the curve takes an abnormal shape, the value of K beginning to decrease more steeply. If this is due to the protonation, the distribution coefficients should enable an estimation of the base strength of acetone.

The pK value of the conjugate acid of acetone, or more strictly, the H_0 value of half-protonation, is given by

$$pK_{AH^+} = H_0 + \log([AH^+]/[A])$$

If K_0 denotes the distribution coefficient of the unprotonated form and if the concentration of the protonated form is negligible in the organic phase, one obtains

$$K_0/K - 1 = [AH^+]/[A]$$

A method to calculate K_0 is to use an equation based on experimental values of K at acidities in which acetone still remains unprotonated. In 45 to 70 % sulfuric acid, the data give an accurate fit to the empirical equation

$$H_0^2 + 10.575 H_0 K_0 + 10.131 H_0 + 23.22 K_0 + 48.41 = 0$$

If this equation is approximately valid for K_0 also in the range in which the protonation occurs, one can calculate the following pK values for the conjugate acid of acetone, as interpolated for equal H_0 intervals:

H ₀	pK _{AH⁺}
-6.60	-7.3 ₂
-6.80	-7.2 ₀
-7.00	-7.3 ₁
-7.20	-7.3 ₆
-7.40	(-7.4 ₈)
-7.60	(-7.6 ₀)

At relatively high acidities the calculated pK 's show a trend to lower values. An obvious reason is that the empirical extrapolation function becomes less accurate when used for relatively long extrapolations. In addition, small amounts of mesityl oxide may be formed interfering with the experimental determination of K when relatively high sulfuric acid concentrations are approached.⁷

The pK value estimated above, -7.3, is in a substantial agreement with the value of -7.2, calculated by Campbell and Edward⁸ from independent indicator measurements.

1. Sadek, H., Abu Ejamayem, M. S. and Abu Elgheit, M. *Suomen Kemistilehti B* **37** (1964) 33.
2. Haldna, U. and Palm, V. A. *Dokl. Acad. Nauk SSSR* **135** (1960) 667.
3. Campbell, H. J. and Edward, J. T. *Can. J. Chem.* **38** (1960) 2109.
4. Kankaanperä, A. *Ann. Univ. Turku. Ser. A I* (1966). *To be published.*
5. Paul, M. A. and Long, F. A. *Chem. Rev.* **57** (1957) 1.
6. Long, F. A. and McDevit, W. F. *Chem. Rev.* **51** (1952) 119.
7. Nagakura, S., Minegishi, H. and Stanfield, K. *J. Am. Chem. Soc.* **79** (1957) 1033.

Received March 1, 1966.

A Note on the Constitution of the Diterpene $C_{20}H_{28}O_3$ from *Solidago canadensis* L.

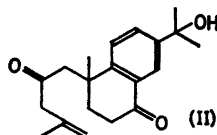
THORLEIF ANTHONSEN

Organic Chemistry Laboratories, Norway
Institute of Technology, Trondheim, Norway

In 1947 Houston and Burrell¹ described a diterpene $C_{20}H_{28}O_3$ (I) from the roots of *Solidago canadensis* L. The m.p. of the primary crystals was 89–90°C, changed to 131–132°C on recrystallisation. The diterpene was devoid of carbonyl functions and did not react with metallic sodium in benzene.

During investigations of members of Compositae for acetylenes *S. canadensis* also has been investigated. The plant was seemingly devoid of acetylenes, but the diterpene described by Houston and Burrell was isolated in good yields and was studied by spectroscopic methods and some preliminary chemical reactions also were carried out.

In a recent note Gerlach² reports investigations on the same diterpene (I) and proposes the constitutional formula (II).



It is remarkable that formula (II) gives $C_{20}H_{28}O_3$, $M = 314$, whereas Gerlach's own analysis agrees with that given by Houston and Burrell, $C_{20}H_{28}O_3$, $M = 316$, and this is also found by Gerlach's mass spectroscopic measurement. We have obtained the same molecular peak 316 and so the $C_{20}H_{28}O_3$ formula for (I) is fully confirmed.

Although our spectroscopical data mostly agree well with those of Gerlach, our interpretation does not allow any of the elements contained in (II).

The UV-spectrum of (I) has one sharp band at 222 $m\mu$ (Gerlach gives 224 $m\mu$) quite incompatible with formula (II), which would be expected to show strong absorption in the 295 $m\mu$ and 250 $m\mu$ ranges (expected ϵ about 2000 and 14 000).

Our NMR-spectrum, cf. Fig. 1, agrees as to position of the bands to the values given

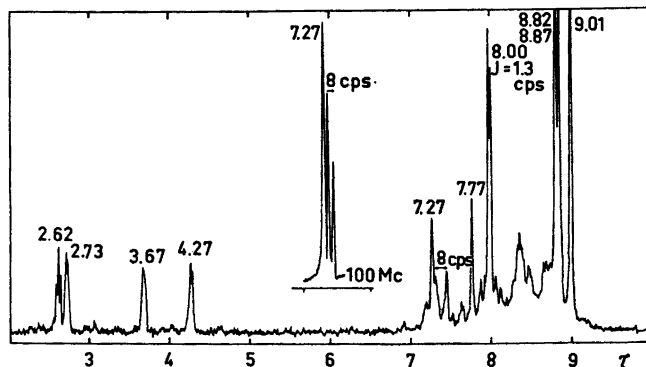


Fig. 1. NMR-spectrum of *Solidago* diterpene $C_{20}H_{28}O_3$ in $CDCl_3$; 60 Mc, Varian A 60; 100 Mc, Varian HA 100.