Studies on Mercury(II)oxide Chlorides and Mercury(II)oxide

KARIN AURIVILLIUS

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

Several mercury(II)oxide chlorides have been described in literature, viz. $Hg_{n+1}O_nCl_2$ with $n = \frac{1}{2}$, 1, 2, 3, 4, 5, 6, and 7 [1]. In the course of studies of these substances the compounds with $n = \frac{1}{2}$, 2, 3, and 4 have been synthetized and investigated by X-rays.

Hg_3OCl_4. Colourless cubes. The cube edge $a = 9.24$ Å and space group $P2_13$ are found in accordance with the data recently reported by Weiss *et al.* [2]

$Hg_3O_2Cl_2$. Black plates. Space group $P2_1/c$. Unit cell dimensions $a = 6.316$ Å, $b = 6.865$ Å, $c = 6.858$ Å, $\beta = 114°\ 24'$ were in accordance with measurements by Gawrych [3]. The observed density 8.8 indicates a cell content of two formula units of $Hg_3O_2Cl_2$. The positions of the mercury atoms have been derived from projections of the Patterson function and corrected by "trial and error" methods giving

2 Hg in 2(a): 0, 0, 0

4 Hg in 4(e): $\pm(x,y,z), \pm(x,\frac{1}{2}+y,\frac{1}{2}-z)$

with $x = 0.425$, $y = 0.360$, $z = 0.265$.

It does not seem possible to arrive at a final decision on the arrangement of the chlorine and oxygen atoms from geometrical considerations. Attempts to attack the problem by means of Fourier methods are in progress.

$Hg_4O_3Cl_2$. Yellow needle-shaped crystals, apparently identical with the mineral kleinite (kindly supplied by Professor F. Wickman, Swedish Museum of Natural History, Stockholm).

$Hg_5O_4Cl_2$. Red crystals which form flat pyramides. Symmetry $P2_1/c$. Unit cell dimensions $a = 10.6$ Å, $b = 9.0$ Å, $c = 11.4$ Å, $\beta = 110°$.

A determination of the crystal structure of mercury(II)oxide was carried out by Zachariasen [4] on the basis of powder photographs. Weissenberg photographs of single crystals of montroydite and synthetic material, however, indicate a larger unit cell.

HgO. Space group $Pnma$. $a = 6.60$ Å, $b = 3.51$ Å, $c = 5.50$ Å. The positions of the mercury atoms are in fair agreement with those given by Zachariasen and it may

be that the superstructure is due to the arrangement of the oxygen atoms.

These investigations and also studies on mercury(II)oxide bromides are continued. Full reports will appear elsewhere.

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Acid-Induced Hydrogen Exchange in Benzene Derivatives as Electrophilic Aromatic Substitution

STIG OLSSON and LARS MELANDER

Nobel Institute of Chemistry, Stockholm 50, Sweden

Qualitative evidence, presented particularly by Ingold *et al.*[1], has shown that the hydrogen exchange induced by acids in benzene derivatives has the characteristics of an electrophilic aromatic substitution, *i. e.* a replacement of H+ by H+. As quantitative measurements of the directing power of several substituents have been carried out for the common types of electrophilic aromatic substitution, especially nitration, it should be of interest to investigate the same influence on the hydrogen exchange.

Preparations of toluene, containing tracer amounts of toluene carrying tritium in its *ortho*, *meta*, *para*, and *alpha* positions, respectively, were shaken with 81.8 % sulphuric acid at 25° C and the decay of the tritium content of the toluene was measured as a function of time. The experiments with the *alpha* substituted toluene showed that the methyl hydrogens do not exchange appreciably with the acid during the reaction times in question (maximum about two days). The results obtained with toluene-2-t, -3-t, and -4-t are shown in Figs. 1 and 2. From the initial slopes of the semilogarithmic curves the rates of tritium exchange were obtained [2], as the integrated rate expression cannot be used owing to the lack of
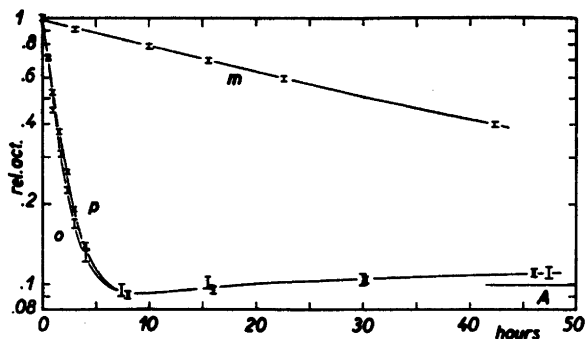
Fig. 1. Semilogarithmic plot of relative specific activity of toluene-2-t (o), -3-t (m), and -4-t (p) as a function of time (3 ml of toluene shaken with 20 ml of 81.8 % sulphuric acid at 25° C). Horizontal line (A) indicates final activity if distribution were uniform between nuclear positions and acid.

knowledge of the exact final equilibrium distribution of tritium in the system. The sulphonation reaction, proceeding with a speed of about 0.5 % of the toluene per hour, makes it impossible to wait for complete equilibrium to be attained. In principle the equilibrium could also at least approximately be found by means of the initial growth rate in a similar experiment with the tritium initially present in the acid. Such experiments were carried out, but for experimental reasons the accuracy was not high enough for an exact determination of the initial slope of the curve.
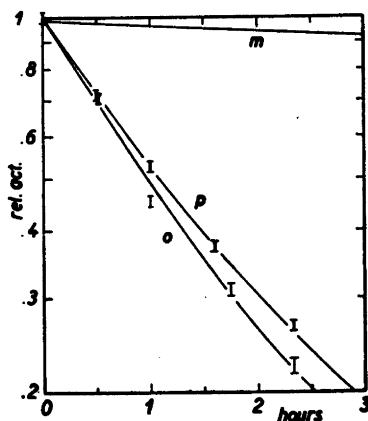

Fig. 2. Part of the same plot as in Fig. 1.

A probable isotope effect in sulphonation [3] will have little influence on the present measurements, since the sulphonation rate given above will be distributed among the different positions in much the same ratio as the exchange rates. Thus the exchange in each position should be very far advanced before an appreciable fraction of the toluene has been sulphonated in that position. Isotopic substitution will certainly have an appreciable effect only on the sulphonation in the same position, and sulphonation in non-triterated positions will not change the specific activity. The only possible influence of importance could be the change in the composition of the acid phase. The acid is present, however, in a tenfold excess over the toluene, and no indications of such an influence have been observed.

The relative exchange rates for tritium in the individual positions of toluene are $o:m:p = (32 \pm 2):(1.00 \pm 0.06):(29 \pm 2)$. The growth curve of the activity in toluene (when tritium was initially present in the acid) is in rough agreement with these figures, although no distinction between the ortho and para positions can be made from this composite curve.

The trend of both kinds of curves for long exchange times seems to indicate that the heavy isotope prefers the position in the aromatic nucleus to that in the acid.

The rate ratio given above is probably approximately valid for all hydrogen isotopes, as spectroscopic data [4,5,6] make it probable that the isotope effect on rate is

not very different for different positions in toluene.

Experiments of the same kind are planned for other benzene derivatives, among which are those containing a bulky alkyl group causing a possible steric hindrance. Homogeneous exchange mixtures should be used in order to enable comparisons between the exchange rates of different kinds of molecules, especially for relating other rates to that of unsubstituted benzene. Experiments with deuterium as tracer are also planned in order to reveal the influence of isotopic mass on the absolute magnitude of the exchange rates and if possible to find differences in isotope effect between different aromatic positions.

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Isolation of α-Methoxy-$\Delta^{\alpha,\beta}$— butenolide from *Narthecium ossifragum* (L.) Huds.

ARNULV STABURSVIK *

Institutt for organisk kjemi, Norges Tekniske Högskole, Trondheim, Norway

A new unsaturated γ-lactone has been isolated from a methanolic extract of the flowering parts of *Narthecium ossifragum*. After removal of carotenoids and accompanying substances, *i.a.* 22-hydroxycholesterol[1], by dilution with water and subsequent extraction with petroleum ether, the diluted methanolic extract was evaporated under reduced pressure. From the residual concentrated aqueous solution further impurities were removed by extrac-

* Research fellow of *Norges Almenvitenskapelige Forskningsråd.*

tion with ether. The lactone could then easily be extracted with chloroform, and, on spontaneous evaporation formed large crystals, which after purification melted at 57° C. (Found: C 52.4; H 5.25. Calc. for $C_5H_6O_3$: C 52.6; H 5.30). M (by titration) 114. Calc. 114. $[\alpha]_D^{20} \pm 0°$. The substance contained one methoxyl group; it failed to give an acetyl derivative. The I.R. spectrum indicated a γ-lactone and an $-O-C = CH-$ grouping[2]. The U.V.-spectrum showed a maximum at 224 mμ, log ε 3.88, indicating an a,β-unsaturated lactone, this structure also being supported by the modified Legal reaction of Paist et al[3].

The most likely structure for the lactone would be a-methoxy- $\Delta^{a,\beta}$-butenolide or β-methoxy-$\Delta^{a,\beta}$-butenolide. As the previously known β-methoxy compound[4] could be excluded because of its higher m.p. (67°), the synthesis of the a-methoxy compound was attempted.

a-Ketoparaconic acid ethyl ester was prepared by the method of Fischhof[5] and decarboxylated according to Schinz and Hinder[6]. The resulting crude ethereal extract, containing a-keto-butyrolactone, was methylated with diazomethane. The oily reaction product on sublimation (100°, 10 mm), crystallisation from ether and resublimation furnished colourless prisms which melted at 57°, undepressed by the natural substance. The I.R. spectra (in chloroform solution) were identical, thus confirming the identity of the two substances. This lactone is stable and forms a striking contrast to a-methoxy-β-methyl-$\Delta^{a,\beta}$-butenolide, which according to[6] liquefies in two months.

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