amount of starting material not recovered) of a neutral, crystalline product of m.p. 87–103°. A sample after being dried at 90° over anhydrous calcium chloride, then crystallized from anhydrous ethyl acetate, had m.p. 100.4–103°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.8. Found: C, 65.66; H, 10.94.

After standing exposed to the air for a few days the analytical sample showed m.p. 87–97°, whereupon it was suspected that the large melting point range of the crude material was due to the formation of an unstable hydrate. Accordingly a sample of the crude material was crystallized once from water to yield crystals of m.p. 87–97°. This material was analyzed.

Anal. Calcd. for $(C_8H_{16}O_2)_2 \cdot H_2O$: C, 62.71; H, 11.18. Found: C, 63.00; H, 11.61.

This compound is assigned the structure of *trans*-1,3-dimethyl-1,3-cyclohexandiol on the basis of its behavior toward boric acid (see below). The possibility that the large melting-point range of this diol was due to contamination by *cis*-1,3-dimethyl-1,3-cyclohexandiol was disposed of by comparison of infrared spectra. Both the crude oxidation product (m.p. 87–103°) and the analytical samples of the anhydrous form (m.p. 100.4–103°) and the hemihydrate (m.p. 87–97°) showed distinctive, strong bands at 10.87 and 9.05 μ which were not present in the spectrum of pure *cis*-1,3-dimethyl-1,3-cyclohexandiol (see below). The only absorption bands near these positions in the *cis* isomer were at 11.05 and 9.14 μ; the minima associated with which fell at 10.70 and 9.02 μ, respectively, close to the positions of the strong bands in the *trans* isomer.

When a 0.20-g. sample of anhydrous *trans*-1,3-dimethylcyclohexandiol (m.p. 100.4–103°) was heated with an excess of boric anhydride at 90° and 30 mm. in a micro-sublimation apparatus, an oil collected on the cold-finger. This oil did not give a qualitative test for boron, reduced permanganate solution instantly, showed a band at 6.2 μ in the infrared indicative of unsaturation, and gave analytical figures indicating that partial dehydration had occurred. It was not further investigated.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 74.78; H, 10.98.

Oxidation of the Low-boiling 1,3-Dimethylcyclohexanol.—Under the standard conditions the low-boiling 1,3-dimethylcyclohexanol reduced an equimolar amount of permanganate in 3 days. After separating unreacted starting material, a continuous ether extract of the aqueous reaction mixture yielded 31% (based on unrecovered starting material) of crystalline material which melted at 88.9–90.0° after crystallization from petroleum ether (b.p. 35–36°)–ethyl acetate.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.55; H, 11.09.

This diol is assigned the structure of *cis*-1,3-dimethyl-1,3-cyclohexandiol. Neither the crude oxidation product nor the analytical sample of the diol showed significant absorptions at 10.87 or 9.05 μ where the *trans* isomer has strong bands.

When 0.20 g. of this diol was heated in a sublimation apparatus with an excess of boric anhydride at 90° and 30 mm., white crystals collected on the cold-finger. These were crystallized three times from petroleum ether (b.p. 35–65°) and dried to yield the borate VII, m.p. 93.4–95.2°. The substance gave a strong test for boron (solution in methanolic sulfuric acid followed by ignition).

Anal. Calcd. for $C_8H_{15}O_3B$: C, 56.50; H, 8.90. Found: C, 56.85; H, 8.82.

Titration curves for the borate (9.0 mg.) and boric acid (1.6 mg.) in 5 ml. of water using sodium hydroxide were identical, so it was concluded that the cyclic borate VII is rapidly hydrolyzed to its components.

Stanford, Calif.

[Contribution from the Chemistry Division, Oak Ridge National Laboratory, Operated by Union Carbide Corp. for the U. S. Atomic Energy Commission, Oak Ridge, Tenn.]

Studies Involving Isotopically Labeled Formic Acid and its Derivatives.[1] VI. Estimation of the Relative Ionization Constants of Formic Acid and Formic-*d* Acid at 24.0 ±0.5°

By Gus A. Ropp

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The ratio of the ionization constants of formic acid and formic-*d* acid (DCOOH) in aqueous solution at 24.0 ± 0.5° was found to be $K_a(H)/(K_a(D) = 1.06 \pm 0.03$. The value of this secondary equilibrium deuterium isotope effect is not consistent with the suggestion of Halevi[4] that the previously observed[5] secondary deuterium isotope effect in the case of the ionization constant of α,α-dideuteriophenylacetic acid is the result of stronger *inductive electron* release from C–D than from C–H bonds.

Introduction

The mechanism of operation of secondary deuterium isotope effects has recently aroused considerable interest.[2,3] Halevi approached the problem by way of studies of the ionization constants[4] of deuterated organic compounds.

In connection with studies of ion–molecule reactions (ref. 1 (III) and (IV)) in formic acid and formic-*d* acid (DCOOH) in the mass spectrometer, we have sought information about the effect of deuterium substitution on the electron displacement toward the oxygen atoms in formic acid. An estimate of the effect of deuterium substitution on the ionization constant of formic acid in aqueous solution at 24.0 ± 0.5° has been made.

Halevi and Nussim[5] reported that the two deuterium atoms in α,α-dideuteriophenylacetic acid, $C_6H_5CD_2$ COOH, lowered the ionization constant of phenylacetic acid about 12% at 25°; the ionization constant of α-deuteriophenylacetic acid, C_6H_5-CHD COOH, should therefore be about 6% smaller than that of phenylacetic acid. Halevi[4] suggested that the measured effect[5] of deuterium on the ionization constant is due to a greater *inductive electron release* of a deuterium atom on the electron displacement toward the oxygen atoms of the carboxyl group as compared with a hydrogen atom. The *inductive effect* of a substituent (in this case a deuterium atom) is well known to increase markedly

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(1) Other papers in this series: This Journal, (I) **73**, 5573 (1951); (II) **79**, 4944 (1957); (III) **80**, 3509 (1958); (IV) **80**, 5573 (1958); (V) **82**, 842 (1960).

(2) W. H. Saunders, Jr., S. Ašperger and D. H. Edison, *ibid.*, **80**, 2421 (1958).

(3) Symposium on Hyperconjugation, University of Indiana, June, 1958.

(4) E. A. Halevi, *Tetrahedron*, **2**, 175 (1957).

(5) E. A. Halevi and M. Nussim, *Bull. Res. Council Israel*, **5A**, 263 (1956).

as the substituent is moved closer to the reaction center.[6] Since the deuterium atom in formic-*d* acid is one atom closer to the oxygen atoms than is the deuterium atom in α-deuteriophenylacetic acid, a greater lowering of the ionization constant by deuterium substitution would accordingly be expected for formic-*d* acid than for α-deuteriophenylacetic acid. From the 6% lowering of the ionization constant in the latter acid, a lowering of the ionization constant of formic-*d* acid of at least 15% is predicted[6] assuming that the influence of deuterium in each acid is exerted *solely through an inductive mechanism*.

Experimental

Formic-*d* Acid.—Formic-*d* acid samples of >95% purity were synthesized by deuterolysis of sodium cyanide as previously described (ref. 1 (III)). Formic acid, C.P. 98–100%, was used in three titrations. In two titrations formic acid of >95% purity, prepared by hydrolysis of sodium cyanide, was used. Since the hydrolysis and the deuterolysis were carried out in the same way, the formic acid prepared from cyanide served as a control to demonstrate that the observed difference between the ionization constant of formic acid and that of formic-*d* acid was not due to a difference in methods of preparing the two acids.

Titrations.—For each determination a 10-λ sample of acid was dissolved in 15 ml. of freshly boiled distilled water and titrated with 0.01 *N* sodium hydroxide in a laboratory where the temperature was maintained at 24.0 ± 0.5°. The Beckman model M *p*H meter used was checked at frequent intervals against a standard buffer solution of *p*H 4.00. The *p*H at 50% neutralization from the complete titration curve was taken to be equal to pK_a. This method does not give a highly accurate estimate of either ionization constant individually. However, it is reasonable to assume that most of the error inherent in the method should cancel in the calculation of the ratio of the ionization constants of formic acid and formic-*d* acids for two reasons. First, care was taken to treat both acids in identically the same manner experimentally; second, formic acid and formic-*d* acid are very nearly identical in many of their physical and chemical properties.

Table I presents the measured pH values, their means, and the 95% confidence intervals of the means

TABLE I

*p*H VALUES OF FORMIC ACID AND FORMIC-*d* ACID AT HALF-NEUTRALIZATION POINT AT 24.0 ± 0.5°

HCOOH	DCOOH	Source of acid
3.715		From hydrolysis of NaCN
	3.725	Batch 1 from deuterolysis of NaCN
3.70		98% C.P. chemical
	3.745	Batch 2 from deuterolysis of NaCN
3.71		98% C.P. chemical
	3.73	Batch 2 from deuterolysis NaCN
3.70		From hydrolysis of NaCN
	3.72	Batch 2 from deuterolysis of NaCN
3.71		98% C.P. chemical
	3.74	Batch 3 from deuterolysis of NaCN
3.707 ± 0.006	3.732 ± 0.010	(Mean values and 95% C.I.)

Results and Discussion

From the data of Table I,

$$\log K_a(\mathrm{H}) - \log K_a(\mathrm{D}) = 0.025 \pm 0.012 \text{ (95\% C.I.)}$$

and

$$K_a(\mathrm{H})/K_a(\mathrm{D}) = 1.06 \pm 0.03$$

The difference between the free energies of ionization for the two isotopic species is

$$\Delta F(\mathrm{H}) - \Delta F(\mathrm{D}) = -2.303\, RT\,(0.025 \pm 0.012) = -34 \pm 16 \text{ cal. per mole}$$

Since the deuterium in formic-*d* acid lowers the ionization constant only about 6%, the isotope effect is hardly greater than the isotope effect due to the substitution of one deuterium atom on the α-carbon in phenylacetic acid. It is therefore reasonable to conclude that the anomalously large effect of deuterium substitution in phenylacetic acid *is exerted mainly through some mechanism other than the inductive mechanism* proposed by Halevi.[7]

The question remains: what is the cause of the anomalously large effect of deuterium atoms on the ionization constant of phenylacetic acid observed by Halevi and Nussim?[5] Studies, which are now being considered, of deuterium isotope effects on the ionization constants of other organic acids may help answer this question. However, two tentative explanations can be offered:

I. A comparison of Fisher–Hirschfelder models of formic and phenylacetic acids suggests a possible explanation. Deuterium atoms on the α-carbon of phenylacetic acid can approach somewhat closer to the carboxyl-group oxygen atoms than the deuterium atom in formic-*d* acid can approach the oxygen atoms in that acid. It may therefore be that the effect of deuterium in α,α-dideuteriophenylacetic acid is partly or largely due to a direct interaction between the deuterium atoms and the oxygen atoms of the carboxyl group. For some carboxylic acids it has been shown that the effect of substitution of electronegative groups on the ionization constant is best explained by considering both the inductive effect and the direct electrostatic effect.[8,9]

II. Hyperconjugation in deuterated phenylacetic acid either between the α-hydrogens and the phenyl group or between the α-hydrogens and the oxygen atoms of the carboxyl group might explain the observed effect of α-deuteration on the ionization constant of phenylacetic acid. It is expected that the degree of hyperconjugation would be isotopically-dependent. Hyperconjugation would not be possible in the case of formic acid and formic-*d* acid.

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(6) G. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 203.

(7) A referee has suggested an additional reason for not accepting Halevi's proposal[4] that the C–D bond, due to anharmonicity, is a better electron releaser than a C–H bond: the C–H stretching frequency in the formate ion is significantly less than that in formic acid. Within experimental error, the presently observed effect of deuterium substitution on the ionization constant of formic acid could—according to this argument—be explained as due simply to a difference between isotopic 0-point energy differences in the free acid and in the ion. If this argument is valid, there is no cause to bring in an explanation based on differential inductive effects due to anharmonicity.

(8) J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953).

(9) Jack Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 69.

Hyperconjugation involving the phenyl group might even exert its effect by loosening the α-hydrogen atoms in phenylacetic acid and promoting direct interaction (I) of the α-hydrogens with the carboxyl group oxygen atoms. Were hyperconjugation involving the phenyl group the dominant factor, a smaller isotope effect on the ionization constant would be expected for α-deuterated acetic acid than for α-deuterated phenylacetic acid. The ratio of the ionization constants of acetic acid and α,α,α-trideuterioacetic acid will be reported later.

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[DEPARTAMENTO DE QUÍMICA ORGÁNICA DE BARCELONA, INSTITUTO DE QUÍMICA "ALONSO BARBA," UNIVERSIDAD DE BARCELONA, SPAIN]

Preparation of Highly Strained Aromatic Chlorocarbons. I. A Powerful Nuclear Chlorinating Agent. Relevant Reactivity Phenomena Traceable to Molecular Strain[1]

BY MANUEL BALLESTER, CARLOS MOLINET AND JUAN CASTAÑER

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The preparation of perchlorotoluene and perchloro-*p*-xylene is effected starting from 2,3,4,5-tetrachloro-1-trichloromethylbenzene and 1,4-bistrichloromethylbenzene, respectively, by means of a powerful nuclear chlorinating agent. 1,3,5-Tristrichloromethylbenzene is inert under the same conditions. Chlorination of 2,4,6-trichloromesitylene with chlorine and white light gives 2,4,6-trichloro-1,3,5-trisdichloromethylbenzene and products of chlorinolysis; no perchloromesitylene is isolated. Under similar conditions perchlorotoluene and perchloro-*p*-xylene readily undergo chlorinolysis. 2,3,5,6-Tetrachloro-1-trichloromethylbenzene, 2,5-dichloro-1,4-bistrichloromethylbenzene and 2,3,5,6-tetrachlorobenzoic acid are also reported for the first time. Some significant results related to the preparation and stability of those chlorocarbons are explained on the basis of steric strain and distortion.

Introduction

A number of exhaustive chlorinations of alkylbenzenes starting either from ring[2-9] or side-chain[2,5,9-12] perchlorinated alkylbenzenes have been described. The chlorination either stopped before replacement of the last (alpha or *ortho*) hydrogen atom or chlorinolysis occurred.

The perchlorinations here reported have been accomplished by means of an extremely powerful yet selective nuclear chlorinating agent. Its composition is similar to the one described by Silberrad,[13] *i.e.*, a solution containing sulfur monochloride and anhydrous aluminum chloride in sulfuryl chloride. Apparently, the essential difference consists in the concentration of the catalysts which in the present case is very high.

Results

2,3,5,6-Tetrachloro-1-trichloromethylbenzene.—Perchlorotoluene (IV) was obtained starting from 2,3,4,5-tetrachloro-1-trichloromethylbenzene (III) In the preparation of the latter, as described previously,[5,11] 2,3,5,6-tetrachloro-1-trichloromethylbenzene (II) occurred as a by-product. It was hydrolyzed (90.9% yield) to 2,3,5,6-tetrachlorobenzoic acid, which was subsequently decarboxylated to 1,2,4,5-tetrachlorobenzene. Neither II nor the acid had been described previously. It appears therefore that the compound melting at 101–102° described as II by Nicodemus[14] was something else.

Perchlorotoluene.[15]—Perchlorotoluene (IV) was obtained from III, Perchlorobenzene (V) was also formed and some starting material was recovered. The yield was about 60%. Under stronger chlorinating conditions an increased amount of perchlorobenzene was formed. It was found that under these conditions IV undergoes chlorinolysis.

Perchlorotoluene was hydrolyzed (98% yield) to pentachlorobenzoic acid, which was subsequently decarboxylated to pentachlorobenzene.

Under photochlorinating conditions with chlorine and white light perchlorotoluene is readily and quantitatively converted into perchlorobenzene.

Perchloro-*p*-xylene.—The preparation of perchloro-*p*-xylene (VIII) was performed starting from *p*-bistrichloromethylbenzene (VI). The yield was 71%; neither perchlorobenzene nor 2,3,5-trichloro-1,4-bistrichloromethylbenzene was detected. 2,5-Dichloro-1,4-bistrichloromethylbenzene (VII) melting at 202–204°, was isolated as a by-product. Shorter reaction times gave greater amounts of the latter. This octachloro-

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(1) Part of this work has been sponsored by the Air Research and Development Command (European Office), U. S. Air Force, under the Contract AF 61(052)-141.

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