COMMUNICATIONS TO THE EDITOR

A NEW GROUP OF ISOMORPHOUS COMPOUNDS A_2XO_4

Sir:

X-Ray data show that alkali sulfates $Me^I_2SO_4$ constitute with alkali alkaline earth phosphates $Me^IMe^{II}PO_4$[1] and with calcium orthosilicate Ca_2SiO_4, modified by phosphate as in Bessemer and open-hearth furnace slags, principally at elevated temperatures, a new group of isomorphous compounds A_2XO_4 with a rather simple hexagonal unit cell containing two molecules. The space group D^3_{3d} and the atomic parameters have been determined for glaserite, $K_3Na(SO_4)_2$, the only substance known before to possess this particular lattice.[2]

TABLE I

Substance and temp. range of stability	Lattice dimensions, Å.		
	a_0	c_0	c/a
α-K_2SO_4, above 590°	5.71	7.86	1.375
α-Na_2SO_4(I), above 239°[3]	5.38[4]	7.26[4]	1.350
Glaserite (K, Na)$_2SO_4$, room temp.	5.66[2]	7.33[2]	1.295[2]
α-$CaNaPO_4$, above 680°	5.23	7.13	1.364
α-$CaKPO_4$, above 705°	5.58	7.60	1.360
$SrNaPO_4$	5.48	7.36	1.34
$BaNaPO_4$	5.64	7.35	1.30
Calcium phosphato silicates, $Ca_x(SiO_4, PO_4)$:			
(Ca_2SiO_4, $^1/_2Ca_3(PO_4)_2$)[1,6,7]	5.38	7.05	1.310
(Ca_2SiO_4, $Ca_3(PO_4)_2$)[a]	5.21	6.90	1.32

[a] Allotropic form of silicocarnotite, $5CaO \cdot P_2O_5 \cdot SiO_2$.[5]

The group is expected to include chromates, vanadates, molybdates, tungstates, arsenates, selenates and other compounds A_2XO_4, particularly at elevated temperatures.

The high-temperature forms can be stabilized by the addition of substances which are insoluble in the low-temperature phase and therefore must be precipitated for transformation. More effective than additions of substances A_2XO_4, which are not isomorphous with the low-temperature forms of the compounds A_2XO_4 to which they are added, are compounds which deviate in composition from A_2XO_4, such as compounds A_2XO_3 (for instance carbonates), AXO_4 (for instance, alkaline earth sulfates), $A_3(XO_4)_2$ (for instance, alkaline earth phosphates) or others. Examples are $CaNaPO_4$–Na_2CO_3, $CaKPO_4$–K_2CO_3,[1] Na_2SO_4–Na_2CO_3,[4] Na_2SO_4–$CaSO_4$, Ca_2SiO_4–calcium phosphates and many others. The identity of the X-ray patterns of alleged "binary compounds," "$CaNa_8(SO_4)_5$"[5] or "$K_3Na(SO_4)_2$,"[2] with the pattern of one or both of their components, together with the known phase diagram of these systems, proves they actually are solid solutions of $CaSO_4$ in α-Na_2SO_4 and of Na_2SO_4 in α-K_2SO_4, respectively.

VANADIUM CORPORATION OF AMERICA
NEW YORK, N. Y. M. A. BREDIG

RECEIVED JUNE 27, 1941

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(1) H. H. Franck, R. Frank, E. Kanert and M. A. Bredig, *Z. anorg. allgem. Chem.*, **230**, 1 (1936), and **237**, 49 (1938).

(2) B. Gossner, *Neues Jahrb. Mineral.*, **B**, **57A**, 89 (1928); "Structurbericht," 1913–1928, p. 378.

(3) F. C. Kracek and C. J. Ksanda, *J. Phys. Chem.*, **34**, 1741 (1930).

(4) L. S. Ramsdell, *Am. Mineral.*, **24**, 109 (1939).

(5) R. Klement and F. Steckenreiter, *Z. anorg. allgem. Chem.*, **245**, 236 (1940).

(6) G. Troemel and A. Koerber, *Arch. Eisenhüettenw.*, **7**, 7 (1933).

(7) G. Nagelschmidt, *J. Chem. Soc.*, 865 (1937).

EFFECT OF HYDROCYANIC ACID ON DISULFIDES

Sir:

The formation of mercaptans from disulfides by the action of cyanide in alkaline solution has long been recognized and interpreted as $RS—SR + NaCN \rightarrow RSNa + RSCN$ [I. Mauthner, *Z. physiol. Chem.*, **78**, 28 (1912); also H. T. Clarke in Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 915]. In discussing the mechanism of activation of such proteolytic enzymes as papain, etc., by hydrogen cyanide, Irving, *et al.* [G. W. Irving, T. S. Fruton and M. Bergmann, *J. Biol. Chem.*, **139**, 569 (1941)] pose the question whether a similar reaction can occur also in slightly acid solution since activation can be brought about at *p*H 5.

In an attempt to answer this question cystine and (—S—S—) glutathione were treated with hydrogen cyanide at *p*H 5 and different temperatures. After various time intervals, qualitative and quantitative tests for thiol groups and for cysteine specifically were performed (nitroprusside test, the Sullivan reaction [M. X. Sullivan, *Public Health Repts.*, **44**, 2, 1600 (1929). This method when applied to the determination of cysteine in the presence of cystine was found reliable when the cysteine comprised at least 10%

of the cystine; otherwise too high values are obtained] and the Mirsky and Anson modification of the Folin method) [A. E. Mirsky and M. L. Anson, *J. Gen. Physiol.*, **18,** 307 (1934). Correct values for cystine by this method are obtained only after removal of the hydrogen cyanide. This was achieved by evacuation with oxygen-free nitrogen passing through the capillary].

At 35° a slow formation of cysteine was noted in a 0.1 *M* citrate buffer solution (*p*H 5.0) containing 0.0025 mole of cystine and 0.0625 mole of potassium cyanide and hydrogen chloride per liter; 5% of the cystine was found to be reduced after twenty-four hours, 11% after seventy-two hours, 18% after six days. At 95° with 0.005 *M* cystine and 0.125 *M* hydrogen cyanide the reaction proceeded quite rapidly, the amount of cysteine formed within one hour corresponding to 49% of the cystine used. Further heating up to six hours caused a slow decrease in the yield of cysteine. When a cystine–hydrogen cyanide reaction mixture, after heating to 95° for one hour, was treated with sulfite to reduce any unchanged cystine, no significant increase in color intensity was found (beyond that due to the cysteine already formed), indicating the absence of any unreacted cystine. This, together with the fact that the yield in cysteine never exceeded 50%, is regarded as evidence that hydrogen cyanide, like potassium cyanide, does not cause reduction but "hydrocyanolysis" of the disulfide ($RS—SR + HCN \rightarrow RSH + RSCN$).

When a solution containing 0.01 mmole of (—S—S—) glutathione and 0.25 mmole of hydrogen cyanide was incubated at 35°, 22% of the glutathione was in the thiol form after three days. In the absence of the hydrogen cyanide no detectable amounts ($<0.5\%$) of thiol were formed under the same conditions. Also in control experiments in which the cystine–hydrogen cyanide reaction mixtures were kept at low temperatures (3 and $-10°$) for as long as eight days, no formation of cysteine could be detected. When cystine was heated at 95° and *p*H 5 in the absence of hydrogen cyanide, only 1.5% of the cystine yielded cysteine in six hours (by hydrolysis).

From these experiments it is concluded that hydrogen cyanide at *p*H 5 attacks disulfides, forming thiol groups more slowly but probably by the same mechanism as does potassium cyanide in alkaline solution. It is impossible to decide whether the rate of this reaction at 40° is sufficient to explain the activating effect of hydrogen cyanide on papain, etc., in the presence of small amounts of disulfide–sulfhydryl systems.

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RECEIVED AUGUST 4, 1941

2-PHENYLTETRALONE-1. A CORRECTION

Sir:

In the recently published article, by Plentl and Bogert [THIS JOURNAL, **63,** 989 (1941)], on "The Synthesis of Tricyclic Hydrocarbons Related to Stilbestrol," 2-phenyltetralone-1 is described as though it were a new compound, whereas it has been reported previously both by Newman [*ibid.*, **60,** 2949 (1938); **62,** 872 (1940)], and by Miss Crawford [*ibid.*, **61,** 608 (1939)]. Newman designated his products as "1-keto-2-phenyl-1,2,3,4-tetrahydronaphthalene" in his first paper, and "1,2,3,4-tetrahydro-1-keto-2-phenylnaphthalene" in his second, while Miss Crawford used the name "1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene" in hers. This variation in nomenclature accounts in part for our failure to catch these articles in reviewing the literature. Our apologies are extended to these fellow investigators for this oversight.

While we all used the same initial material, *viz.*, α,γ-diphenylbutyric acid, the methods for its conversion into the tetralone differed. Newman gave the m. p. as 76–77°, Miss Crawford as 79–80°, and our product melted at 79°.

Our statement on page 991 of that article that 2-phenyltetralone-1 "did not react with semicarbazide hydrochloride" should be corrected. We ran the reaction only once, in an alcoholic solution containing sodium acetate as buffer, and failed to insolate a semicarbazone. On repeating the reaction, however, with what little tetralone we had left (38 mg.), we have been more successful, and have obtained a semicarbazone, which proved rather difficult to purify, as it was already somewhat discolored, and then melted at 254° (Anschütz total immersion thermometer), with some prior gas evolution and sintering.

Anal. Calcd. for $C_{17}H_{17}ON_3$: C, 73.1; H, 6.1. Found: C, 73.4; H, 6.4.

Newman, who prepared the semicarbazone without difficulty, found that it melted with decomposition at 250–251.4°, after sintering at 245°.

Our somewhat higher m. p. need not be interpreted, however, as indicating any greater purity, for at high temperatures a difference of 3° is not serious, and our analytical results do not justify any such claim.

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RECEIVED JULY 18, 1941

ADDITION COMPOUNDS OF ZINC, CADMIUM, COBALT AND NICKEL HALIDES WITH 1,4-DIOXANE

Sir:

In a recent paper [THIS JOURNAL, **62,** 3522 (1940)] R. Juhasz and L. F. Yntema describe a series of "Addition Compounds of Zinc, Cadmium, Cobalt and Nickel Halides with 1,4-Dioxane." The great majority of these I prepared already some years ago (H. Rheinboldt, A. Luyken and H. Schmittmann, *J. prakt. Chem.*, **149,** 30–54 (1937); *C. A.*, **31,** 6615 (1937)), *i. e.*, the compounds: $ZnCl_2 \cdot 2(C_4H_8O_2)$, $ZnBr_2 \cdot 2(C_4H_8O_2)$, $ZnI_2 \cdot 2(C_4H_8O_2)$, $CdCl_2 \cdot (C_4H_8O_2)$, $CdBr_2 \cdot (C_4H_8O_2)$, $CdI_2 \cdot (C_4H_8O_2)$, $CoCl_2 \cdot (C_4H_8O_2)$, $CoBr_2 \cdot 2(C_4H_8O_2)$, $CoI_2 \cdot 2(C_4H_8O_2)$ and $NiI_2 \cdot 2(C_4H_8O_2)$.

Besides we described other compounds which belong to the same series: $CoI_2 \cdot 4(C_4H_8O_2)$, $NiCl_2 \cdot 2(C_4H_8O_2)$ and $NiBr_2 \cdot 2(C_4H_8O_2)$.

Further on we described addition compounds of dioxane with certain metal halides: $CaCl_2$, $CaBr_2$, CaI_2, $SrBr_2$, SrI_2, BaI_2, $MgCl_2$, $MgBr_2$, MgI_2, $HgCl_2$, $HgBr_2$, HgI_2, $Hg(CN)_2$, $Hg(CNS)_2$, $CuCl_2$, $CuBr_2$, $SnCl_2$, $SnBr_2$, $MnCl_2$, $MnBr_2$, MnI_2, $FeCl_2$, $FeBr_2$, FeI_2.

In a previous publication (*J. prakt. Chem.*, **148,** 81–87 (1937); *C. A.*, **31,** 4321 (1937)) we described dioxanates of LiCl, LiBr, LiI, NaI, KI and NH_4I.

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H. RHEINBOLDT

RECEIVED JULY 15, 1941

COMPOUNDS OF 1,4-DIOXANE WITH METAL HALIDES

Sir:

In a list of "New Compounds" of zinc, cadmium, cobalt and nickel halides with 1,4-dioxane (THIS JOURNAL, **62,** 3522 (1940)) that had been prepared in this Laboratory (Thesis, St. Louis University, (1934)), there were included a number described by Rheinboldt, Luyken and Schmittmann (*J. prakt. Chem.*, **149,** 30 (1937)). The compounds that should have been reported are as follows (R = 1,4-dioxane): $ZnCl_2 \cdot R$, $CdCl_2 \cdot {}^1/_2R$, $CoI_2 \cdot 3R$, $CoI_2 \cdot R \cdot 2H_2O$, $CoI_2 \cdot R \cdot 4H_2O$, $NiCl_2 \cdot R$ and $NiBr_2 \cdot R$.

The writer is glad to make this correction and assumes responsibility for the error.

DEPARTMENT OF CHEMISTRY
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L. F. YNTEMA

RECEIVED JULY 28, 1941

THE THERMAL DECOMPOSITION OF ACETALDEHYDE

Sir:

It is known that reaction chains may be induced in the thermal decomposition of acetaldehyde by the addition of small amounts of oxygen or other materials, but whether pure acetaldehyde decomposes thermally by a chain mechanism is still a matter of controversy. Recently, Burton, Ricci and Davis [THIS JOURNAL, **62,** 265 (1940)], employing the Paneth technique with radioactive lead, have obtained some positive evidence for radical chains in the thermal reaction. Their work is open to two objections. (1) Even the slightest trace of impurity, for example 0.001% oxygen [Letort, *J. chim. phys.*, **34,** 428 (1937)] would have initiated reaction chains and thus led to a positive result for their experiments. (2) The experiments could not determine what fraction of the acetaldehyde was decomposing by way of the chains.

A method which seemed to offer better possibilities for deciding this question was to decompose mixtures of acetaldehyde and acetaldehyde-d_4. If a chain reaction occurred, such processes as the following would take place

$$
\begin{aligned}
CH_3CHO &\longrightarrow CH_3 + CHO \\
CD_3CDO &\longrightarrow CD_3 + CDO \\
CH_3 + CD_3CDO &\longrightarrow CH_3D + CD_3CO \\
CD_3 + CH_3CHO &\longrightarrow CD_3H + CH_3CO
\end{aligned}
$$

and the methanes produced in the reaction would be mixed as to deuterium content. On the other hand, if the reaction were intramolecular, only CH_4 and CD_4 would be formed. Since Benedict, Morikawa, Barnes and Taylor [*J. Chem. Physics*, **5,** 1 (1937)] have shown that methane and the deuteromethanes may be identified and determined by their infrared spectra, one should be able to evaluate these alternatives through an infrared examination of the products formed in the above experiment.

This has now been carried out. Three hundred millimeters of an equimolecular mixture of acetaldehyde and acetaldehyde-d_4 (99.5%, from Norway) has been decomposed at 535° and the products submitted to infrared examination on the instrument in this Laboratory [Gershinowitz and Wilson, *J. Chem. Physics*, **6**, 197 (1938)]. For comparison purposes a similar sample with 0.04% added oxygen was decomposed at 435° and analyzed in the same way. The results show clearly that in the case of the pure acetaldehydes there is very slight absorption in the regions of characteristic CD_3H and CH_3D frequencies (1100–1300 cm.$^{-1}$, 2205 cm.$^{-1}$), whereas there is very pronounced absorption in these same regions for the mixture to which the trace of oxygen had been added.

These findings demonstrate that there is little or no mixing of the hydrogen and deuterium in the methanes during the thermal decomposition of the acetaldehydes, and therefore that the decomposition must proceed substantially by a molecular mechanism. A preliminary estimate indicates that a minimum of 80% and possibly 100% of the reaction undergoes molecular decomposition.

The experimental details and infrared plates will be presented in a later paper.

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RECEIVED AUGUST 22, 1941

NEW BOOKS

Free Radicals as Intermediate Steps in the Oxidation of Organic Compounds. Volume XL, Art. 2, pages 37–132 of the Annals of the New York Academy of Sciences. By L. FARKAS, MANUEL H. GORIN, L. MICHAELIS, OTTO H. MÜLLER, MAXWELL SCHUBERT, and G. W. WHELAND. The New York Academy of Sciences, care of the American Museum of Natural History, New York, N. Y., 1940. 96 pp. Illustrated. 15.5 × 23.5 cm. Price, $1.25. This monograph is one of several, which, if purchased as a set, may be had at a reduced price.

This volume of six papers, presented at a conference of the Physics and Chemistry section of the New York Academy of Sciences in November, 1939, represents an excellent review of our current knowledge in the field of semiquinones. The title is misleading, however, for the roles of "ordinary" free radicals and semiquinones in organic reaction kinetics are only occasionally touched upon.

The paper by Michaelis, the leader in this field, occupies over one-third of the volume. It gives a broad presentation of the definitive studies that have been carried out in his laboratory together with a detailed presentation of the important principles involved. Twenty figures of experimental data are given and the paper is accompanied by a complete bibliography of 53 titles with the subject matter of each reference indicated. This article is undoubtedly the best review available on the existence of semiquinones, their equilibria with the reduced and oxidized forms and the dimeric meriquinones, their detection by potentiometric, magnetometric, and spectrophotometric methods; and the role of resonance in determining their stability. Michaelis presents the challenging thesis that every (organic) oxidation can proceed only in steps of univalent oxidation.

In an interesting paper Schubert explores the analogy between electron and proton removal from organic compounds. Cases of apparent simultaneous ejection of two protons are rare, but fairly clear-cut examples in titrations of N-alkyl thiazolium and pyridinium compounds are discussed. Reference is made to the significant studies of Schwarzenbach on the state of ionization, symmetry, and resonance of dyestuff molecules; it is regrettable that practically no work has been done along these lines with the semiquinones themselves.

Müller discusses in detail the possibilities of the polarograph in studying semiquinone formation and supports the theories with experimental examples. This technique offers good prospects for extending the potential range into the overvoltage field and for studying systems incompletely reversible. Farkas considers the experimental feasibility of determining the presence of small concentrations of semiquinones by the measurement of the rate of conversion of para-hydrogen to equilibrium hydrogen. This method should give estimates of the semiquinone formation constant k when it is considerably less than the present lower limit of measurement of 0.01, corresponding to about 5% of dyestuff in semiquinone form.

Free radicals are discussed in two papers. Gorin evaluates the standard free energy of the free radical HO_2 in aqueous solution as -3.5 kcal. and that of O_2^- as 9.5 kcal. from estimations of the strengths of electron-pair and three-electron bonds between oxygen atoms. These values, 6 kcal. below the estimates in use derived from kinetic reasoning, are of great importance in interpreting the kinetics of oxygen and peroxide reactions. Wheland reviews qualitatively the calculation of the stability of hydrocarbon free radicals; mathematical difficulties have so far pre-