done on the sciatic nerve of the intact guinea pig according to the method of Shackell.[8]

An insufficient number of animals was used to determine accurately the subcutaneous toxicity in the guinea pig and the intravenous toxicity in the rabbit.

The members of this series of anesthetics appear to be vaso-dilators as determined by intravenous injection in the cat. However, they act synergistically with epinephrine. The relative conductive potency figures shown in Table III are based upon the use of solutions containing various concentrations of each anesthetic, with epinephrine 1:60,000.

The outstanding member of this series of anesthetics is the octyl-2 derivative which we call Octacaine. An examination of Table III shows that octacaine has the highest anesthetic efficiency ratio for surface anesthesia, being 24 times as efficient as cocaine. It is 8 times more efficient as a conductive anesthetic than procaine. The *m*-amino derivatives are considerably less toxic than the corresponding *p*-amino compounds.

Dr. Frank Co Tui, of the New York University School of Medicine, will shortly publish a complete pharmacological report on Octacaine.

Summary

1. Four new members of a series of previously reported β-alkylamino-α,α-dimethylethanols and the salts of the *p*-aminobenzoates are described.

2. A series of β-alkylamino-β,β-dimethylethanols and the salts of the aminobenzoates are also described.

3. A preliminary pharmacological investigation of these anesthetics is reported.

BROOKLYN, NEW YORK RECEIVED JANUARY 20, 1943

[8] Shackell, *Anesthesia and Analgesia*, **14**, 20 (1935).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

The Thermal Diagram of the System Iron–Tin[1,2]

BY W. F. EHRET AND D. H. GURINSKY[3]

Equilibria in the iron–tin system have been studied rather extensively during the last two decades.[4] Wever and Reinecken,[5] using thermal, magnetometric and microscopic methods, concluded that the system possessed two intermetallic compounds, Fe_3Sn and $FeSn_2$. Preece and Edwards,[6] using similar methods, reported three compounds: Fe_2Sn, FeSn and $FeSn_2$. The X-ray work of Ehret and Westgren[7] confirmed the three compounds just mentioned but these investigators found two additional phases, a high temperature modification of FeSn, which they called γ (NiAs structure), and a β' phase at approximately 60% Sn, which corresponds to Fe_3Sn_2. They were not certain whether the latter really was a single phase or a mixture of two. Its lower limit of stability lay between 550 and 600°. In the most recent work on this system, that by Jones and Hoare,[8] alloy samples were heat treated and then examined microscopically. These investigators were able to substantiate the phase diagram of Preece and Edwards, and concluded that the γ phase of Ehret and Westgren did not exist at 68.5% Sn and 850°.

Because of the differences in the conclusions drawn in the above-mentioned reports, the present authors undertook the reëxamination of this system with the view of clarifying the situation so far as it concerned equilibria existing above 500° and in the range of 10 to 100% Sn. It was felt that below 500° the diagram had been correctly established.

Experimental

The rather well-known techniques of heat treating, quenching, and X-ray analysis were employed as the chief means of investigation. Microscopic examination served as an auxiliary means. The alloys were prepared from Wemco research iron[9] and redistilled tin[10] melted together in magnesia crucibles. Most of the melts were made in a

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting, September 9, 1942.

[2] Condensed from the doctoral dissertation of D. H. Gurinsky, October, 1942.

[3] Present address: Metallurgical Laboratories, University of Chicago, Chicago, Illinois.

[4] For a review of all work published to date on the iron–tin system, including practical aspects, the reader is referred to an article on "The Constitution of the Iron–Tin Alloys" by O. E. Romig which appeared in *Metal Progress*, **42**, 899 (1942).

[5] Wever and Reinecken, *Z. anorg. allgem. Chem.*, **151**, 349 (1926).

[6] Preece and Edwards, *J. Iron Steel Inst.* (London), **124**, 41 (1931).

[7] Ehret and Westgren, THIS JOURNAL, **55**, 1339 (1933).

[8] Jones and Hoare, *J. Iron Steel Inst.* (London), **129**, 273 (1934).

[9] Westinghouse Electric and Supply Co., East Pittsburgh, Penna.

[10] Vulcan Detinning Works, Sewaren, N. J.

vacuum furnace, already described by the authors,[11] in which the pressure did not rise above 10^{-2} mm. In some alloys, those between 60 and 80% Sn, layering was encountered as the liquidus cooled. Satisfactory alloys were prepared in this region by heat treating (soaking) mixtures of iron and tin powders in Pyrex or silica tubes for long enough periods of time to permit equilibrium to be established by diffusion, mostly in the solid state. Powder samples for the diffraction analyses were obtained from the solid alloys by one of three methods: grinding on an alundum wheel, crushing in a diamond mortar, or by filing.

Heat treatment of the powdered alloy samples was conducted in a specially constructed vertical tube furnace provided with an arrangement for rapid quenching. The powder samples were mixed with an equal volume of powdered aluminum oxide to prevent the sintering together of small metal fragments. The mixed powders were sealed into silica tubes under vacuum and the tubes were then suspended in the furnace by means of a fine nichrome wire. A falling-weight device permitted quenching the specimens in less than $^4/_{10}$ of a second. The higher temperatures in this work were measured with a Pt–Pt,Rh couple and the estimated error is ±10°. For the lower temperatures a Chromel–Alumel couple with an estimated error of ±4° was used.

The chemical composition of the alloys was found by analyzing for iron by the well-known dichromate method. Diffraction analyses were carried out in focussing cameras[12] using iron K-radiation. These cameras permit the determination of lattice parameters with an accuracy of 1 part per 1000.

Results

Table I lists the compositions of some of the alloys that were prepared, the heat treatments to which they were subjected, and the phases found present in the solids obtained by quenching. From these data and from information obtained by previous investigators the phase diagram shown in Fig. 1 has been constructed. All of the phases in this system, other than the iron and tin, belong to the hexagonal system. The concordance between the observed $\sin^2 \theta$ values and those calculated from the parameters for the several phases as given below is as good as that found by Ehret and Westgren[7] and is consequently not again set out in the form of tables. The following are the lattice constants for the intermetallic phases as found in the present work, beginning with the one richest in iron

Fe_2Sn	$a_0 = 5.449$ Å. $c_0 = 4.347$	$c_0/a_0 = 0.798$
Fe_3Sn_2	$a_0 = 21.32$ $c_0 = 4.381$	$c_0/a_0 = 0.205$
$FeSn$	$a_0 = 5.288$ $c_0 = 4.442$	$c_0/a_0 = 0.840$
γ (NiAs structure)	$a_0 = 4.230$ $c_0 = 5.206$	$c_0/a_0 = 1.231$
$FeSn_2$	Constants identical with those reported by Ehret and Westgren.[7]	

TABLE I

Alloy No.	Sn, % wt.	Annealing temp., °C.	Quenching time, hrs.	Phases present
1	36.2	663	72	αFe, Fe_3Sn_2
2	..	703	315	αFe, Fe_3Sn_2
3	..	782	48	αFe, Fe_2Sn
4	50.3	838	90	Fe_2Sn, γ (s)[a]
5	52.8	670	72	αFe, Fe_3Sn_2
6	..	790	48	Fe_2Sn, Fe_3Sn_2, γ (?)[b]
7	..	820	72	Fe_2Sn, Fe_3Sn_2, Sn (?)
8	..	1016	20 min.	Sn, αFe, γ(?), $FeSn_2$ (tr.)
9	61.0	550	68	FeSn, αFe (tr.)
10	..	596	48	FeSn, αFe (tr.)
11	..	637	70	FeSn, αFe (tr.)
12	..	653	72	FeSn, Fe_3Sn_2
13	..	655	72	FeSn, Fe_3Sn_2
14	..	732	96	Fe_3Sn_2, γ(s), Sn(s)
		782	48	Fe_2Sn_3, γ(s), Sn(s)
15	..	785	92	Fe_3Sn_2, γ(s), Sn(s)
16	..	800	48	Fe_3Sn_2, γ(s), Sn(s)
17	..	826	24	Fe_3Sn_2, γ, Sn(s)
18	..	842	20	Fe_2Sn, γ, Sn(s)
19	..	860	48	Fe_2Sn, γ, Sn(s)
20	..	863	15 min.	αFe, γ, Sn(s)
21	63.6	860	48	γ, Sn(s)
22	66.8	675	70	FeSn
23	..	830	50	Sn, γ, FeSn(?), Fe_3Sn_2(s)
24	69.2	450	28 days, then slow cooled	FeSn, αFe (tr.) $FeSn_2$ (tr.)
25	..	745	27	Fe_3Sn_2, FeSn, Sn
26	..	830	45	γ, Sn, FeSn(s)
27	77.9	450	8 days, then slow cooled	$FeSn_2$, αFe(s) FeSn(s)
28	..	842	24	γ, Sn, FeSn
29	81.5	660	74	FeSn, Sn
30	..	780	96	Fe_3Sn_2, Sn
31	..	845	48	γ, Sn, FeSn(?)
32	..	874	24	γ, Sn
33	..	917	19	αFe, Sn, γ(?)
34	..	1020	25 min.	αFe, Sn

[a] (s) = small amount present as indicated by the intensity of lines on photograms. [b] (?) = In some instances a few lines appeared which might be indexed as belonging to a certain phase. When the question mark is placed alongside of the indicated phase, it is implied that the expected quota of lines was *not* filled.

The accompanying reproduction of powder photograms (Fig. 2) shows the diffraction lines of each of these phases except the last.

Discussion

From the results above it will be seen that, in contradistinction to the earlier report by Ehret and Westgren, we now prefer to use chemical formulas rather than Greek letters to represent the composition of all the intermediate phases except γ. The simplest whole-number ratio of atoms which was nearest the composition of an alloy that contained little more than a single phase was selected as the formula for the compound involved. This seemed justified because the lat-

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[11] Ehret and Gurinsky, *Rev. Sci. Instr.*, **12**, 151 (1941).

[12] Westgren, *Trans. Am. Inst. Min. Met. Eng., Inst. Metals Division* (1931), p. 14.

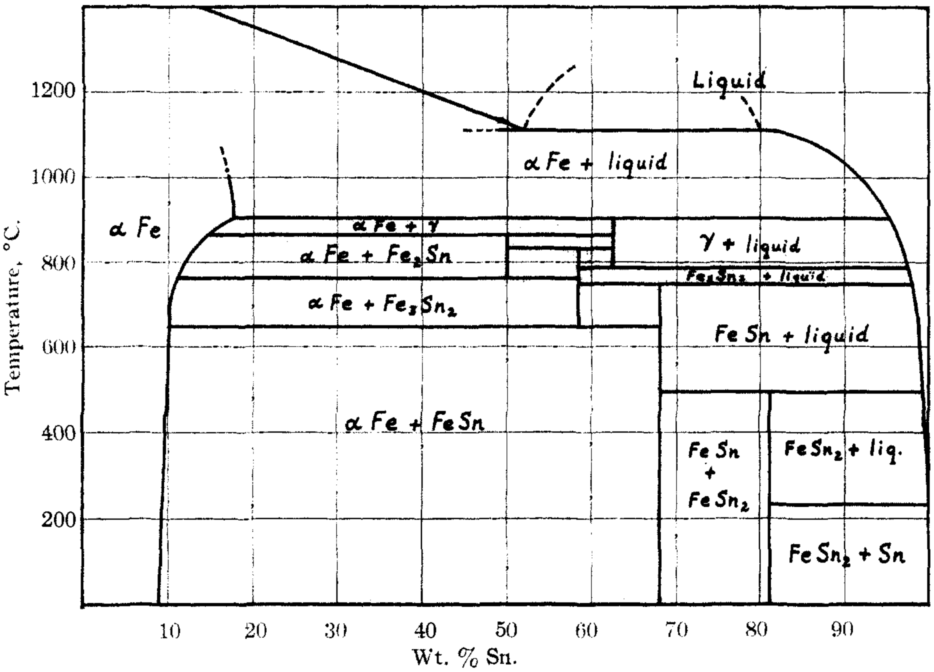

Fig. 1.—Phase diagram for iron–tin alloys.

tice dimensions of the phases are constant. The γ phase (*ca.* 62% Sn) appears to be a complicated solid solution (ideal NiAs structure would require 68.1% Sn), and the Greek letter designation has therefore been retained for it.

In establishing an equilibrium diagram by quenching methods, many experiments must usually be performed in the hope of ascertaining that equilibrium existed before quenching and that no unnoticed changes occurred during the quenching operation. In our own case the number of experiments shown in Table I is only a fraction of those performed. The annealing times given (except for alloys 24 and 27) were found by trial to be sufficient so that no further changes were noticed in our results by extending the time. It may therefore be assumed that the alloys, with the exception of those just mentioned, were in a state of equilibrium before quenching. An examination of Table I shows that some alloys contained three, some even four, phases *after* quenching. It is, of course, possible to have three phases in equilibrium at a particular temperature in a system of this sort but the probability of its happening is small, consequently one must look elsewhere for an explanation of the presence of three phases after quenching. The presence of four phases definitely shows lack of equilibrium after quenching.

In Fig. 1 the authors have attempted to include not only those results which represented a successful quenching of an equilibrium but also those in which a reaction occurred during the quenching operation thus producing additional phases. The manner in which each of the alloys contributed in the construction of the diagram will now be considered in some detail. The first five alloys seem to represent two-phase equilibria that have been successfully quenched down. Alloy no. 6 contains the two phases one would expect from our equilibrium diagram, *i. e.*, Fe_2Sn and Fe_3Sn_2; there are in addition a few lines on the diffraction pattern which seem to belong to the γ phase but other significant lines of this phase are missing. The meaning of these lines is not apparent at the moment. The same may be said of alloy no. 7. The appearance of some $FeSn_2$, and perhaps some of the γ-phase, in the quenched sample of alloy no. 8 is an indication, the authors believe, that this phase (or phases) was deposited from the tin-rich liquid during the quenching interval. Alloys no. 9 through 13 represent two-phase equilibria that have been quenched down without difficulty. Alloys no. 14 and 15 are indicative of an invariant system at approximately 782°. Here Fe_3Sn_2, γ, and liquid are in equilibrium. The phases which the liquid must deposit on cooling are apparently insufficient in amount to produce

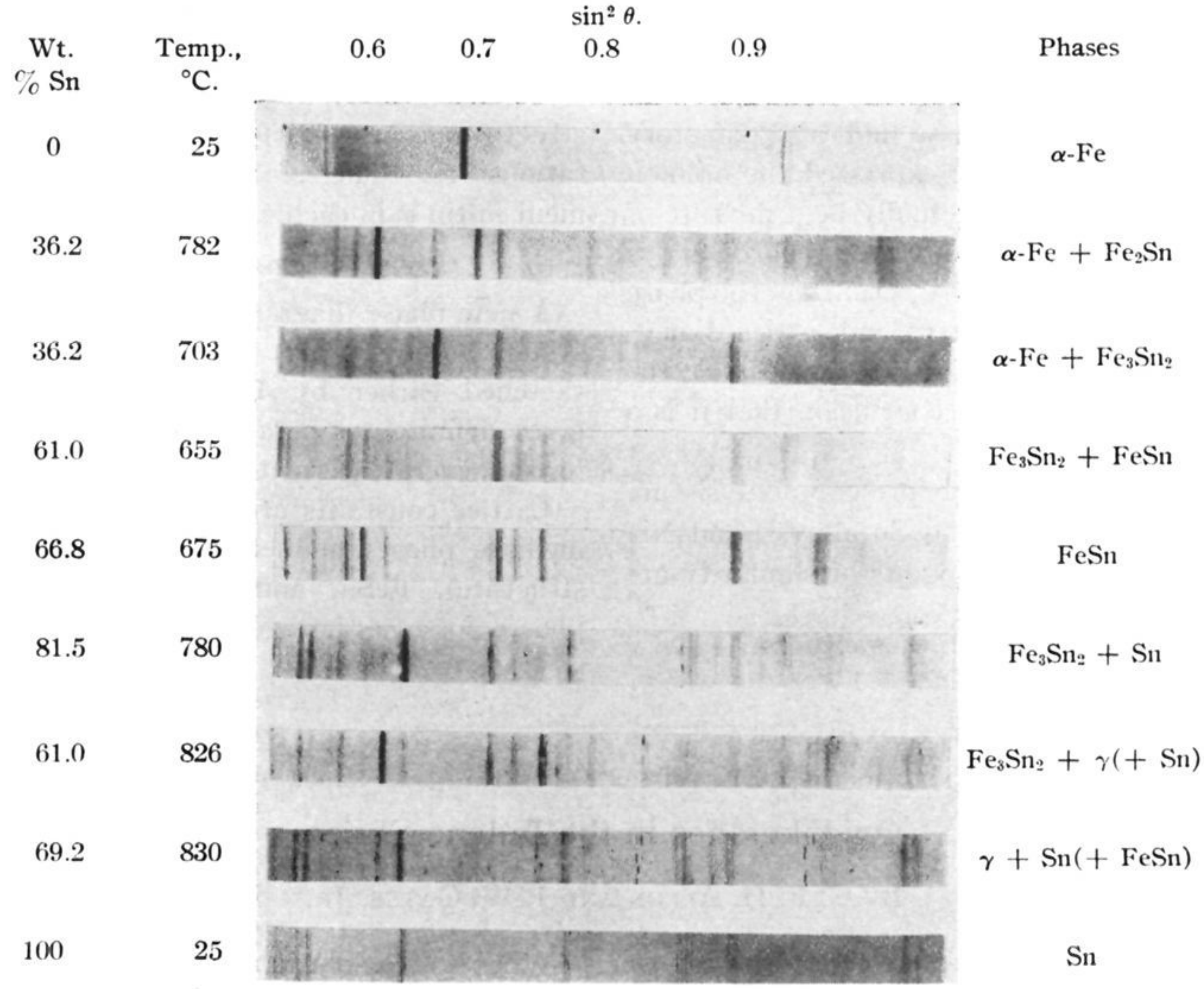

Fig. 2.—Powder photograms of Fe–Sn system.

observable diffraction effects. Alloys no. 16 and 17 seem to reflect high temperature equilibrium between Fe_3Sn_2 and the γ phase. The latter decomposes slightly during quenching thus giving rise to tin. Alloys no. 18 and 19 are similar to 16 and 17 except that Fe_2Sn is in equilibrium with the γ-phase at the temperatures shown. In order to account for the presence of small amounts of tin one must again assume that the γ phase decomposes slightly during the quenching act. Such decomposition should presumably also give rise to some Fe_3Sn_2, but the latter was not observed. This may have been due to the fact that the diffraction lines of Fe_3Sn_2 are always weak, even when it is present in large proportion. Alloy no. 20 represents a similar situation except that we are now above the upper temperature limit for Fe_2Sn. Alloy no. 21, according to the reasoning just advanced, corresponds to the γ-phase at 860° or it may have a slightly higher tin content than this phase. Alloy no. 22 shows that the FeSn phase is stable at least up to 675°. Alloy no. 23 apparently corresponds to an equilibrium at 830° between the γ phase and tin-rich liquid. The slight decomposition of the former upon quenching accounts for the Fe_3Sn_2 that is present. If any FeSn is present in this alloy, it would be due to deposition from the liquid upon cooling. Alloy no. 24, like 27, is one in which equilibrium was almost attained. A repetition of the experiment, with longer annealing, did not seem justified since the results were in complete accord with the rather well-established lower reaches of the equilibrium diagram. Alloy no. 25 indicates an invariant system at 745°. This is apparently the upper temperature limit for the existence of FeSn. Alloy no. 26 seems to correspond to a two-phase equilibrium between the γ phase and tin-rich liquid at 830°. The small amount of FeSn is deposited by the liquid as it is quenched. Alloy no. 28 is interpreted in a similar manner. Alloys no. 29 and 30 fall into two-phase regions in the diagram. Alloy no. 31 is analogous to 28, and no. 32 is similar to 31. Alloy no. 33 is similar to no. 8 and some of the γ-phase may be present for the same reason as mentioned under no. 8. Alloy no. 34 is readily interpreted in terms of the diagram.

Comparison of the earlier report[7] with this one shows only minor differences in lattice dimensions except for the Fe_3Sn_2 phase for which Ehret and Westgren were not able to find a satisfactory unit cell, in fact they had expressed the opinion that this "phase" might actually be a mixture of two. To test the latter point we prepared alloys richer, respectively, in iron and tin than the phase itself. Its diffraction pattern and lattice dimensions remained substantially unchanged in the new alloys, leading to the conclusion that it is a single phase.

When the results of the present analysis are compared with those for Co–Sn alloys[13] and Ni–Sn alloys,[14] the following points of similarity are noted: Each of the systems possesses one phase with nickel arsenide structure. The structures of CoSn and FeSn appear to be identical. Complex structures appear in each system when the atomic ratio is 3:2. The solubility of the transition element in tin is in each case negligibly small.

Summary

A new phase diagram has been set up for the system iron–tin. It confirms the diagram sketched earlier by Ehret and Westgren and gives definite temperature intervals of stability for the several intermetallic phases.

Lattice constants are given for the five intermediate phases, namely, Fe_2Sn, Fe_3Sn_2, γ(NiAs structure), FeSn, and $FeSn_2$. Each of these phases possesses hexagonal symmetry.

New York, N. Y. Received December 31, 1942

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[13] Nial, *Z. anorg. allgem. Chem.*, **238**, 287 (1938).

[14] Mikulas, *et al.*, *Trans. Am. Inst. Min. Met. Eng., Inst. of Metals Division*, (1936), p. 124.

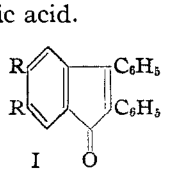
[Contribution No. 905 from the Kodak Research Laboratories]

Oxidoketones in the Indene Series

By C. F. H. Allen and J. W. Gates, Jr.

Since the polyphenylindenones, the chemical behavior of which has been examined by us for some years,[1,2] are α,β-unsaturated ketones, it would be expected that some reactions, characteristic of this linkage, would be found. However, owing to the high degree of substitution, any reactions subject to this sort of hindrance, such as halogen addition, would be suppressed. Up to now, only reduction has been observed to take place, resulting in an indanone.

Alkaline hydrogen peroxide forms oxidoketones with many α,β-unsaturated ketones,[3,4] a reaction apparently unhindered by substitution, and applicable to cyclic compounds.[3] 2,3,5,6-Tetraphenylindenone I gives an oxidoketone II (R = C_6H_5) with this reagent. Like all members of this class of substances, it shows peroxidic properties, liberating iodine from potassium iodide in acetic acid.



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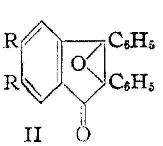

II

When a cold solution of the oxidoketone in acetic acid is treated with dry hydrogen chloride in acetic acid, a white substance (III) is formed, that on warming in the same solvent with mineral acid is transformed into a lactone. The lactone is soluble in alkaline hydroxides, but not carbonates, and careful acidification gives an acid, which on warming alone or in solution, regenerates the lactone. Oxidation of both the acid and the lactone gives 4,5-diphenyl-2-benzoylbenzoic VI and benzoic acids. The structures are thus established as IV (R = C_6H_5) for the lactone and V (or its tautomer) for the acid.

The lactone IV (R = C_6H_5) acts normally with the Grignard reagent, addition of two equivalents giving rise to the ketones VII, VIII (R = C_6H_5); the expected tertiary alcohol could not be isolated when methylmagnesium iodide was used. Since the lactone is isomeric with the oxidoketone, rearrangement seems to have taken place. However, the isolation of an intermediary substance III (R = C_6H_5) enables one to establish the mechanism of the reaction.

The empirical formula of the intermediate differs from that of the oxidoketone by the addition of one molecule of water. It is well known that ethylene oxides are easily cleaved under acidic conditions, and that the products are open-

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[1] Allen and Gates, This Journal, **64**, 2120, 2123, 2127, 2439 (1942).

[2] Allen and VanAllan, *ibid.*, p. 1260 (this gives the earlier references).

[3] Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).

[4] Kohler, Richtmyer and Hester, This Journal, **53**, 205 (1931).