

TABLE IV
DEBYE-SCHERRER PATTERN OF NaCl-TYPE SnP AND
CALCULATED INTENSITIES FOR NaCl-TYPE AND
SPHALERITE-TYPE SnP ($\lambda(\text{Cu K}\alpha)$ 1.54178 Å,
 $a = 5.535 \pm 0.001$ Å)^a

I/I_0 obs.	h	k	l	d (obs.)	d (calc.)	I calc. (NaCl type)	I calc. (Sphalerite type)
90	1	1	1	3.2177	3.1955	84	159
100	2	0	0	2.7748	2.7674	123	44
85	2	2	0	1.9599	1.9568	89	89
50	3	1	1	1.6703	1.6688	38	68
45	2	2	2	1.5996	1.5977	31	11
20	4	0	0	1.3847	1.3837	14	14
15	3	3	1	1.2704	1.2698	15	27
40	4	2	0	1.2377	1.2376	38	14
25	4	2	2	1.1300*	1.1298	29	32
10	5	1	1	1.0649*	1.0651	9	16
15	4	4	0	.9784*	.9784	11	11
15	5	3	1	.9351*	.9355	16	29
20	6	0	0	.9225*	.9224	5	2
20	6	2	0	.8751*	.8751	24	24
5	5	3	3	.8441*	.8440	10	17
15	6	2	2	.8343*	.8344	29	11
						R = 18.4%	R = 51.0%

^a Asterisks signify $\lambda(\text{Cu K}\alpha)$ 1.54051 Å.

Discussion

The formation of two new high-pressure forms of SnP has been shown. It is unclear which phase is the more stable at 65 kbars and why the two phases are intimately mixed. X-Ray diffraction at high pressure may perhaps resolve the phase relationships. The cubic phase should be the high-pressure phase since the density is greater. The calculated density of the cubic phase is 5.860 g/cm³ while the calculated density of the tetragonal phase is 5.68 g/cm³. The cubic form may be present at high pressure and upon quenching may revert partially to the tetragonal phase. The transformation

from tetragonal to cubic upon heating at atmospheric pressure is interesting since it involves a transformation from a less dense to a more dense phase.

The crystal structure of the tetragonal phase has been shown to be similar to that of high-pressure GeP and GeAs.⁹ The structure (Figure 1) is related to the NaCl type by a small shifting of atoms. If the diagonal on the basal plane equaled the *c* axis and $z = 0.5$, the structure would be NaCl type. The atoms are in a distorted octahedral arrangement having one short bond, four slightly longer equal bonds, and one long bond. The shift to the cubic structure involves a regularization of the octahedron. The crystal structure of SnAs⁸ is known to be NaCl type and implies that as the elements become more metallic the NaCl-type structure is favored. Both forms of SnP are metallic conductors. This may be because the compounds have one extra electron for conduction. The tetragonal forms of GeP and GeAs showed superconductivity;⁹ however, only the cubic SnP was seen to be superconducting above 1.25° K.

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A Kinetic Study of the Reaction of Arsenic Acid with Iodide Ions

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The rate of the reaction of arsenic acid with potassium iodide was studied at 25.0° and at ionic strengths 0.200, 0.300, and 3.00 *M*. The rate equation, obtained by a statistical treatment of the data, is $V = k_1[\text{H}^+][\text{H}_3\text{AsO}_4][\text{I}^-] + k_2[\text{H}^+]^2[\text{H}_3\text{AsO}_4][\text{I}^-] + k_3[\text{H}^+]^2[\text{H}_3\text{AsO}_4][\text{I}^-]^2$. The reaction shows very low salt effects even in the presence of Ba²⁺ ions. The catalytic effect of iron(II) and copper(I) ions was also investigated. The reaction mechanism is discussed.

The reaction between arsenate and iodide ions in acidic media was studied by several authors¹⁻⁴ by different techniques, but until now a satisfactory interpretation of the results has not been given either because the experimental methods¹ were inadequate or because it was not the main object of the research.²⁻⁴ Roebuck¹ was able to show that the reaction orders extrapolated to zero concentration of the reactants were unity for every reactant and greater than unity for I⁻

and for H⁺ in more concentrated solutions of these ions. Liebhafsky³ and Bobtelsky and Rosowskaja-Rossienskaja⁵ arrived at the same conclusion.

Experimental Section

The chemicals used for the kinetics were Na₂HAsO₄·7H₂O (Erba RP), KI (Erba RP), and HClO₄ (Erba RP, 60%). The sodium perchlorate used to keep the ionic strength, *I*, constant in part was a BDH LR product purified by recrystallization and in part was prepared from HClO₄ and Na₂CO₃ (Erba RP) and then recrystallized twice from water. NaClO₄ was standardized by neutralization after it passed through acidic ion-exchange resin.

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(4) J. N. Wilson and R. G. Dickinson, *J. Am. Chem. Soc.*, **59**, 1358 (1937).

(5) M. Bobtelsky and R. Rosowskaja-Rossienskaja, *Z. Anorg. Allgem. Chem.*, **190**, 346 (1930).

TABLE I
INITIAL REACTION RATE, V ,
AT VARIOUS REACTANT CONCENTRATIONS^a

Run ^b	$10[\text{H}^+]$ M	$10[\text{I}^-]$ M	$10^3[\text{H}_3\text{AsO}_4]$ M	10^3V_{exptl} $M \text{ sec}^{-1}$	10^3V_{calcd} $M \text{ sec}^{-1}$	% error ^c
1	0.05	0.25	0.50	0.102	0.060	(+41)
2	0.10	0.25	0.50	0.171	0.124	(+28)
3*	0.10	0.80	0.0502	0.057	0.041	(+28)
4*	0.10	0.80	0.225	0.30	0.185	(+37)
5	0.20	0.25	0.50	0.29	0.26	+12.0
6*	0.20	0.80	0.0694	0.130	0.123	+5.0
7*	0.25	0.80	0.304	0.83	0.70	+15.0
8	0.30	0.25	0.50	0.44	0.40	+9.0
9	0.50	0.025	0.50	0.067	0.068	-1.8
10	0.50	0.05	0.50	0.134	0.137	-2.5
11	0.50	0.10	0.50	0.28	0.28	-0.4
12	0.50	0.20	0.50	0.57	0.57	-0.6
13*	0.50	0.20	0.180	0.21	0.21	+3.3
14*	0.50	0.20	0.361	0.40	0.41	-4.0
15*	0.50	0.20	0.721	0.86	0.83	+3.4
16*	0.50	0.20	1.80	2.1	2.1	+3.6
17*	0.50	0.20	2.70	3.2	3.1	+3.7
18*	0.50	0.20	9.01	11.0	10.3	+5.8
19*	0.50	0.20	13.5	16.6	15.5	+6.3
20*	0.50	0.20	18.00	22.5	20.7	+8.0
21	0.50	0.25	0.20	0.26	0.29	-12.4
22	0.50	0.25	0.30	0.42	0.44	-5.0
23	0.50	0.25	0.50	0.72	0.73	-1.2
24	0.50	0.25	0.75	1.00	1.09	-9.4
25	0.50	0.25	1.00	1.52	1.46	+4.1
26	0.50	0.25	1.50	1.95	2.19	-11.9
27	0.50	0.25	2.00	3.0	2.9	+1.4
28	0.50	0.25	2.50	3.7	3.6	+2.3
29	0.50	0.25	3.00	4.4	4.4	+0.2
30	0.50	0.25	5.00	8.3	7.3	+11.8
31	0.50	0.30	0.50	0.90	0.89	+1.0
32	0.50	0.50	0.50	1.58	1.57	+0.6
33*	0.50	0.60	0.361	1.34	1.39	+3.9
34	0.50	0.75	0.50	2.5	2.5	-0.0
35*	0.50	0.80	0.0901	0.46	0.49	-7.9
36*	0.50	0.80	0.361	1.89	1.96	-3.9
37	0.50	1.00	0.50	3.3	3.6	-10.3
38*	0.50	1.20	0.361	3.2	3.3	-2.8
39	0.50	2.00	0.50	8.9	9.0	-0.4
40*	0.60	0.20	0.373	0.53	0.53	-1.1
41*	0.60	0.80	0.0932	0.60	0.65	-8.5
42*	0.70	0.20	0.382	0.64	0.66	-3.3
43*	0.70	0.80	0.0955	0.73	0.82	-12.5
44	0.75	0.25	0.50	1.29	1.20	+7.0
45	1.00	0.25	0.50	1.70	1.73	-1.9
46*	1.00	0.80	0.10	1.29	1.42	-10.0
47*	1.25	0.20	0.409	1.52	1.49	+2.0
48	1.50	0.05	0.50	0.55	0.52	(+4.0)
49*	1.50	0.10	0.415	0.73	0.90	(-23.4)
50	1.50	0.10	0.50	1.11	1.09	+2.5
51	1.50	0.25	0.50	3.1	3.0	+2.4
52*	1.50	0.30	0.415	2.6	3.1	(-20.4)
53	1.50	0.50	0.50	7.1	7.0	+0.3
54*	1.50	0.80	0.415	9.4	10.9	(-16.1)
55*	1.50	1.00	0.415	14.4	15.0	(-4.6)
56	1.50	1.00	0.50	19.3	18.1	+6.2
57	1.50	2.00	0.50	65	52	+19.6
58*	1.70	0.20	0.419	2.4	2.3	(+4.5)
59	2.00	0.25	0.50	4.4	4.6	-3.7
60	2.50	0.25	0.50	6.9	6.4	+6.9
61*	3.00	0.20	0.432	6.3	5.6	(11.2)
62*	3.00	0.80	0.108	8.8	8.9	(-2.0)

^a Temperature 25.0°; $V = -d[\text{H}_3\text{AsO}_4]/dt \text{ M sec}^{-1}$. ^b Asterisks refer to the runs at $I = 0.2 \text{ M}$ (NaClO_4) (except where required by the reactant concentrations) whereas the other runs were carried out at $I = 0.3 \text{ M}$ (NaClO_4). ^c % error = $[(V_{\text{exptl}} - V_{\text{calcd}})/V_{\text{exptl}}] \times 100$. The errors were calculated using for V_{exptl} and V_{calcd} a number of significant figures greater than the one reported in the table. The errors in parentheses correspond to runs not included in the statistical treatment.

A small amount of EDTA (10^{-5} M) was present in all the runs to avoid any possible catalysis by traces of heavy-metal ions. Except at $[\text{H}^+] \geq 0.15 \text{ M}$ the kinetics was followed by repeated titrations of the iodine with the dead-stop method previously described.⁶ The runs at high acidity were usually carried out adding some starch as an indicator because under these conditions the electrodes were always partially depolarized, leading to

inaccurate results. However, even at $[\text{H}^+] \geq 0.15 \text{ M}$ some runs were performed with the dead-stop method. For consistency they were not included in the statistical treatment. The presence of an excess of thiosulfate was avoided with the usual⁶ care in order to minimize the effects of the arsenate-thiosulfate reaction which, mainly at the high hydrogen ion concentrations, became important. All the measurements have been carried out under conditions of constant stirring, after saturating the solutions with very pure nitrogen, to avoid the presence of oxygen traces. The temperature was in all cases 25.0°. Some preliminary runs showed that the reaction was not sensitive to light and to the presence of arsenite ions. All the measurements were repeated at least twice and in all cases the agreement was of the order of 5%. The values of $V = d[\text{H}_3\text{AsO}_4]/dt$ reported in the tables have been calculated from the initial rates (*ca.* 4%) obtained by plotting the amount of added thiosulfate against time.

The emf measurements at $I = 3.00 \text{ M}$, to determine the dissociation ratio of H_3AsO_4 , were carried out with a Metrohm Herisau Model E 388 pH meter. The glass electrode had the KCl bridge replaced by NaCl, to avoid erratic readings due to KClO_4 precipitate.⁷ The pH meter was standardized against solutions of known HClO_4 concentrations keeping the ionic strength constant with NaClO_4 . The dissociation ratio of H_3AsO_4 was also measured, at $I = 3.00 \text{ M}$, by an indicator method using *p*-nitroaniline. HClO_4 - NaClO_4 solutions were again used as standards, and the $[\text{H}^+]$ was determined by spectrophotometry, using a Uvispek Model H 700 spectrophotometer and a wavelength of 391 $m\mu$.

Results

Table I reports the rates, V , obtained at ionic strengths 0.200 and 0.300 M , NaClO_4 being the added salt. A preliminary statistical analysis shows that there are no significant differences in the rates at the two ionic strengths; therefore all these data are considered together.

To calculate $[\text{H}^+]$ and $[\text{H}_3\text{AsO}_4]$ from the stoichiometry, the dissociation constant of the arsenic acid, measured by Washburn and Strachan,⁸ is used, corrected for the effects of the ionic strength by means of the Güntelberg⁹ equation for the activity coefficients.

At first sight the order of the reaction appears to be 1 with respect to the arsenic acid (see runs 12-20 and 21-30) and higher than 1 for hydrogen (see runs 1, 2, 5, 8, 23, 44, 45, 51, 59, 60; 14, 40, 42, 47, 58, 61; 35, 41, 43, 46, 62) and iodide ions (see runs 9-12, 23, 31, 32, 34, 37, 39; 48, 50, 51, 53, 56, 57; 14, 33, 36, 38). The orders with respect to H^+ and I^- , measured by the usual method of the dilogarithmic plots, appear not to be constant. Plotting $V/[\text{H}^+]$ against $[\text{H}^+]$, the concentrations of arsenic acid and iodide being constant, and $V/[\text{I}^-]$ against $[\text{I}^-]$, the concentrations of arsenic acid and hydrogen ion being constant, approximate straight lines of positive slopes and positive intercepts are obtained (see Figure 1). This is evidence for several reaction paths, some of which have orders greater than

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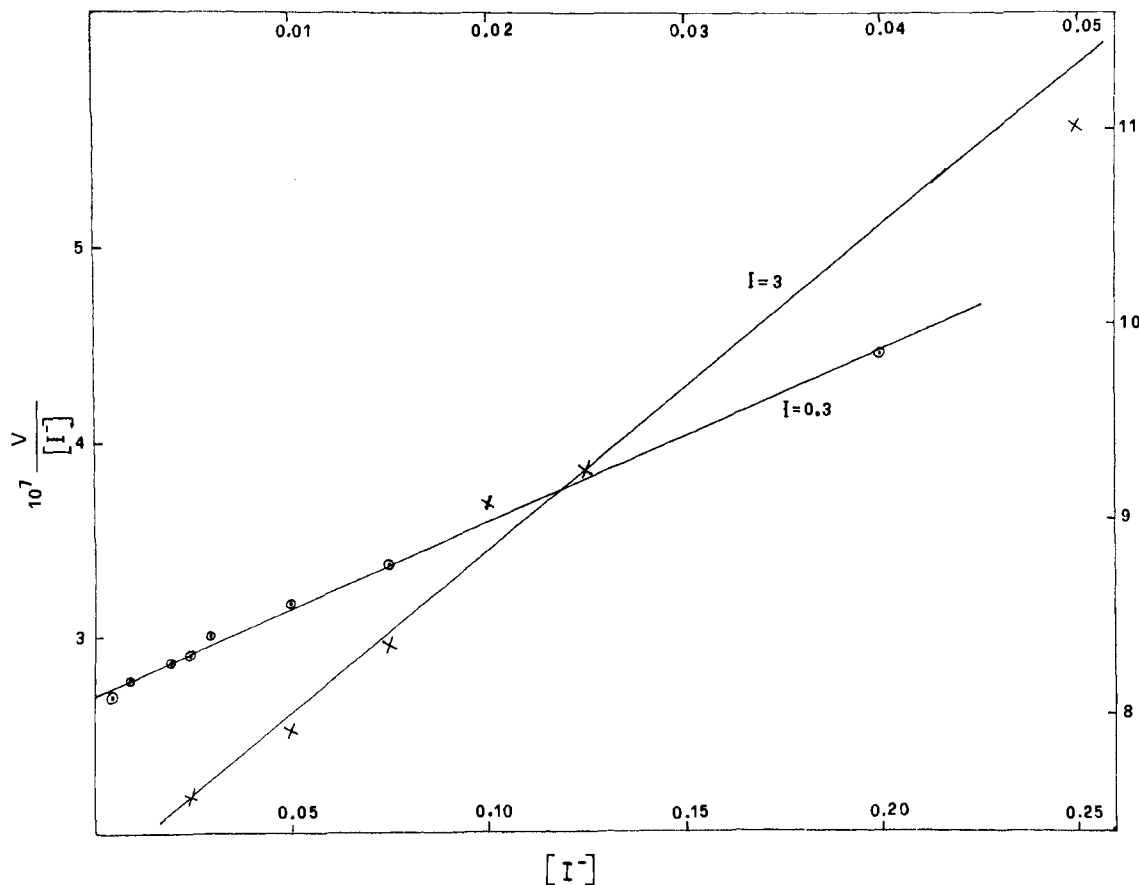


Figure 1.—Rates divided by the I^- concentrations plotted against I^- concentrations. Circles: $I = 0.300 M$, $[H^+] = 0.05 M$, $[H_3AsO_4] = 0.005 M$ (left and lower scales). Crosses: $I = 3.00$, $[H^+] = 0.055 M$, $[H_3AsO_4] = 0.0050 M$ (right and upper scales).

unity with respect to H^+ and I^- . A three-parameter equation which satisfactorily fits the data for $0.02 M \leq [H^+] \leq 0.25 M$ is

$$V = k_1[H^+][H_3AsO_4][I^-] + k_2[H^+]^2[H_3AsO_4][I^-] + k_3[H^+]^2[H_3AsO_4][I^-]^2 \quad (1)$$

and the values of the parameters found by statistical analysis (see Appendix) are $k_1 = (0.95 \pm 0.03) \times 10^{-3} M^{-2} \text{ sec}^{-1}$, $k_2 = (0.26 \pm 0.04) \times 10^{-2} M^{-3} \text{ sec}^{-1}$, and $k_3 = (0.71 \pm 0.06) \times 10^{-1} M^{-4} \text{ sec}^{-1}$. Other equations give significantly worse fittings. However for $[H^+] < 0.02 M$ the rates calculated from eq 1 are significantly lower than the experimental ones (runs 1-4) and this suggests that a term $k_0[H_3AsO_4][I^-]$ gives some contribution at low $[H^+]$. It is not very useful, however, to report a value for k_0 , due to the experimental difficulty of obtaining precise data at low acidity. It is not surprising that this less important path has escaped the attention of previous workers.¹⁻⁴ The path of first order with respect to each reagent is always the most important one in the explored range of concentrations. Nevertheless the paths of superior order are perfectly meaningful, and the deviations from overall order 3 that they give cannot be attributed to the medium effects. In fact the changes in the composition are quite low and a change in the ionic strength from 0.200 to 0.300 M does not lead to important differences.

Another similar series of runs was performed in

3 M $NaClO_4$. The H^+ and H_3AsO_4 concentrations are calculated from the ratio $Q = [H^+][H_2AsO_4^-]/[H_3AsO_4]$ determined by emf and spectrophotometric measurements. The agreement between the results of the two methods is satisfactory and a mean value of $4.76 \times 10^{-3} M$ is obtained for Q . Extreme values are 3.75×10^{-3} and $5.33 \times 10^{-3} M$, and even the use of either of these does not change the H^+ and H_3AsO_4 concentrations significantly. The rates in this medium are reported in Table II, and the values of the rate constants are $k_1 = (2.33 \pm 0.01) \times 10^{-3} M^{-2} \text{ sec}^{-1}$, $k_2 = (0.96 \pm 0.02) \times 10^{-2} M^{-3} \text{ sec}^{-1}$, and $k_3 = 0.42 \pm 0.07 M^{-4} \text{ sec}^{-1}$. These are remarkably greater than the ones corresponding to $I = 0.200$ or $0.300 M$. It should be noticed that the activity coefficients of ions in the presence of swamping electrolytes are often unpredictable.¹⁰

Salt Effects.—Table III gives the rates at different concentrations of various salts. Although, according to the Brønsted theory¹¹ the reaction paths included in eq 1 should be sensitive to changes in ionic strength, the effect of I is not very marked. In fact, by passing from $I = 0.112 M$ to $I = 0.300 M$, a decrease in the rate of 14% is observed, instead of about 27% as calculated using the Güntelberg equation.

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TABLE II
INITIAL REACTION RATE, V ,
AT VARIOUS REACTANT CONCENTRATIONS^a

Run	$10[\text{H}^+]$, M	$10[\text{I}^-]$, M	$10^3[\text{H}_3\text{-AsO}_4]$, M	$10^8 V_{\text{exptl}}$, $M \text{ sec}^{-1}$	$10^8 V_{\text{calcd}}$, $M \text{ sec}^{-1}$	% error ^b
1	0.050	0.25	0.500	0.33	0.161	(+52)
2	0.100	0.25	0.500	0.46	0.34	(+27)
3	0.200	0.25	0.500	0.77	0.68	+11.1
4	0.200	0.05	0.500	0.139	0.128	+7.7
5	0.207	0.20	0.302	0.32	0.34	-5.3
6	0.502	0.25	0.200	0.86	0.84	+2.1
7	0.503	0.50	0.300	2.61	2.9	-11.8
8	0.509	0.25	1.000	4.3	4.3	+0.6
9	0.518	0.25	2.006	9.4	8.8	+6.5
10	0.550	0.05	0.504	0.38	0.41	-8.7
11	0.550	0.10	0.504	0.79	0.86	-8.1
12	0.550	0.20	0.504	1.82	1.84	-1.4
13	0.550	0.25	0.504	2.3	2.4	-2.9
14	0.550	0.50	0.504	5.5	5.56	-1.0
15	0.608	0.10	1.001	2.1	1.93	+7.3
16	0.802	0.25	0.317	2.6	2.5	+2.5
17	0.803	0.05	0.500	0.69	0.66	+4.6
18	1.032	0.10	0.300	1.10	1.16	-6.2
19	1.050	0.25	0.501	6.1	5.8	+5.0
20	1.502	0.05	0.500	1.52	1.53	-1.3
21	2.050	0.25	0.500	17.7	16.5	+6.7

^a Temperature 25.0°; $I = 3.00 M$ (NaClO_4); $V = -d[\text{H}_3\text{AsO}_4]/dt M \text{ sec}^{-1}$. ^b % error = $[(V_{\text{exptl}} - V_{\text{calcd}})/V_{\text{exptl}}] \times 100$. The errors were calculated using for V_{exptl} and V_{calcd} a number of significant figures greater than the ones reported in the table. The errors in parentheses correspond to runs not included in the statistical treatment.

TABLE III
INITIAL REACTION RATE ($M \text{ SEC}^{-1}$) IN THE PRESENCE
OF SEVERAL ADDED SALTS AT 25°

	I, M			
	0.112	0.300	0.800	1.00
NaClO_4	1.81×10^{-8}	1.59×10^{-8}	1.50×10^{-8}	1.43×10^{-8}
NaNO_3	1.81×10^{-8}	1.55×10^{-8}	1.45×10^{-8}	1.37×10^{-8}
NaCl	1.81×10^{-8}	1.54×10^{-8}	1.53×10^{-8}	1.31×10^{-8}
$\text{Ba}(\text{ClO}_4)_2$	1.81×10^{-8}	1.65×10^{-8}	1.41×10^{-8}	1.31×10^{-8}
	I, M			
	10^{-4}	10^{-8}	10^{-2}	
$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	1.99×10^{-8}	1.84×10^{-8}	1.61×10^{-8}	
FeSO_4	1.81×10^{-8}	1.80×10^{-8}		
CuSO_4	3.70×10^{-8}	3.97×10^{-8}		

Table III reports also the rate measurements in the presence of iron(II) and of the traces of copper(I) ions which remain in solution in the presence of Cu_2I_2 . Whereas the ferrous ions do not seem to exhibit catalytic effects,⁶ in the presence of copper ions a remarkable increase in the rate is observed. In each run is observed a very rapid initial development of iodine, due to the reaction between Cu^{2+} and I^- ions, with formation of Cu_2I_2 precipitate. When an amount of iodine equivalent to the amount of cupric ions added is developed, the reaction rate suddenly decreases giving the values in Table III. If it is assumed that the catalytic action depends upon a redox intermediate reaction of the added ion, its presence in the case of copper(I) ions and its absence for iron(II) ions agree with respective redox normal potentials.¹²

Discussion

The present results may be compared with those obtained by Roebuck¹ and by Wilson and Dickinson⁴ with regard to the first-order reaction path with respect to each reactant. The value calculated by Lieb-

hafsky³ on the basis of Roebuck's data for k_1 , extrapolated at 25°, is $0.95 \times 10^{-3} M^{-2} \text{ sec}^{-1}$, in exact agreement with our value for k_1 , and may be regarded in satisfactory agreement with Wilson and Dickinson's value of $1.18 \times 10^{-3} M^{-2} \text{ sec}^{-1}$ ⁴ obtained by isotopic exchange measurements. This path can be explained with the rapid equilibrium between a neutral molecule of arsenic acid and hydrogen ion; the product reacts further with an iodide ion giving H_3AsO_3 and $\text{I}(\text{I})$. Since arsenic acid in acid media exchanges very rapidly its oxygens with the water,¹³ it seems impossible to tell whether the product of the equilibrium is H_2AsO_3^+ or H_4AsO_4^+ . We prefer the latter formulation because in aqueous solutions cations are likely to be highly hydrated.

The mechanism of the path involving two H^+ and one I^- may be interpreted as a reaction of the iodide ion with a diprotonated form of the arsenic acid. The most difficult question however is why there is a path which is second order with respect to I^- only if it is at the same time at least second order with respect to H^+ . A reasonable interpretation is that there is a rapid preequilibration involving the formation of a reactive five-coordinate As(V) intermediate. This is followed by a rate-determining reduction step which can take place by an intramolecular elimination of IOH if the arsenic acid is monoprotated (term k_1). If the arsenic acid is diprotonated or even more protonated, an attack by an I^- ion from the solution can compete with this elimination which is retarded by the lower electron density on the oxygens. On the other hand the formation of the five-coordinate intermediate occurs to an increasing extent when increasing the degree of protonation of the arsenic acid because of the increased positive charge and of the decrease of the electron density on the arsenic.¹⁴ The net result of the reduction by elimination of IOH is the transfer of an OH^+ from arsenic acid to the I^- with formation of IOH. This is similar to the mechanism proposed by Edwards¹⁵ for the reactions of many peroxides with different nucleophiles and to the reaction of SO_3^{2-} with ClO_3^- studied by Halperin and Taube.¹⁶ We suggest that in these reactions as well the mechanism can be more complicated than a nucleophilic attack on the oxygen. The fact that ClO_2^- is an oxidant for SO_3^{2-} much better than ClO_3^- ¹⁶ is hardly reconcilable with the greater basicity of ClO^- which would make this ion a much worse leaving group than ClO_2^- .

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Appendix

Most of the data at $I = 0.200$ and $0.300 M$ were treated together to find the equation giving the best fitting. Some data reported in Table I were excluded because $[H^+]$ was less than $0.02 M$ (runs 1-4) or because, since $[H^+] \geq 0.15 M$, the rates were measured by the dead-stop method which under those conditions could give erroneous results. For these runs the per cent errors in Table I are in parentheses.

Since the *relative* errors in the rates were approximately constant, the general treatment consisted of minimizing the expression

$$\sum d^2 = \sum \left(1 - \frac{V_{\text{calcd}}}{V_{\text{exptl}}} \right)^2 \quad (2)$$

This was obtained using the "Gauss normal equations."¹⁷ For V_{calcd} the following equations were tried

$$V_{\text{calcd}} = \sum_n k_n [H^+]^p [H_3AsO_4]^q [I^-]^r \quad (3)$$

with $q = 1$ in all cases. For p and r the following sets of values were tried: for $n = 3$

$$(p,r) = (1,1; 1,2; 2,1) \quad (3a)$$

$$= (1,1; 2,1; 2,2) \quad (3b) = (1)$$

for $n = 4$

$$(p,r) = (0,1; 1,1; 2,1; 2,2) \quad (3c)$$

$$= (1,1; 1,2; 2,1; 2,2) \quad (3d)$$

for $n = 5$

$$(p,r) = (0,1; 1,1; 1,2; 2,1; 2,2) \quad (3e)$$

The equation

$$V_{\text{calcd}} = k_1 [H^+] [H_3AsO_4] [I^-] + \frac{k_2 [H^+]^2 [H_3AsO_4] [I^-]^2}{1 + k_3 [I^-]} \quad (4)$$

was also tested. In this case the Gauss normal equations were no longer applicable and a method of trial and error was used. A tentative value of k_3 was introduced and the values of k_1 and k_2 were found by minimizing $\sum d^2$ with respect to k_1 and k_2 using the normal equations. $\sum d^2$ was calculated and then the entire procedure was repeated with a new value for k_3 . According to the change observed in $\sum d^2$, a new, better value of k_3 could be chosen and so on, until finally the value of k_3 was chosen which gave the minimum $\sum d^2$.

The ability of the various equations to represent the experimental data could be checked using the χ^2 test¹⁸

$$\chi^2 = \sum \frac{d^2}{\sigma^2}$$

where σ is the *a priori* standard deviation of the experimental values. This quantity can be roughly evaluated as amounting to 0.05 from the results of

repeated runs. However as a superior limit for σ the value of

$$s_{\text{opt}} = \sqrt{\frac{\sum d_{\text{opt}}^2}{N - n_{\text{opt}}}} \geq \sigma$$

can be taken, where d_{opt} are the values of $[1 - V_{\text{calcd}}/V_{\text{exptl}}]$ for the equation with n parameters which gives the optimum fit, and N is the number of experimental runs. The optimum equation, among the ones tested, is (3e), but since this contains a negative k we use as s_{opt} the one obtained from (3c) which amounted to 0.064. The resulting values of χ^2 for the various three-parameter equations are: (3a), 109.4; (3b) = (1), 57.1; (4), 95.0. For 47 degrees of freedom the values of χ^2 corresponding to 0.90 and 0.995 are, respectively, 59.8 and 75.7.¹⁸ This means that eq 3b, although it is not as good as (3c), cannot be ruled out with a probability greater than 90%, whereas (3a) and (4) can be ruled out with a probability greater than 99.5%. Other equations, which were tried, give a χ^2 even greater.

For (3d) and (3e), which have an acceptable χ^2 , the k 's corresponding to $(p,r) = (1,2)$ are definitely negative and therefore meaningless as rate constants, so that no path second order with respect to I^- and first order with respect to H^+ gives an appreciable contribution. The fact that they are not zero probably means that there is an appreciable contribution of a path which is second order with respect to I^- and third order with respect to H^+ . Although (3c) does not give a fit much better than (3b), an indication that a path with $(p,r) = (0,1)$ may be significant is given by the fact that the results at very low $[H^+]$ (runs 1-4) are predicted much better by (3c) than by (3b) although the corresponding parameters are obtained *not* including runs 1-4 in the treatment. However since the values at low $[H^+]$ are less reproducible and may also be affected by a reverse reaction, it is not very useful to include these runs in the statistical treatment and to report a numerical value for the k corresponding to a zero order with respect to H^+ .

Equation 4 leads to a reaction mechanism which is more common than the one which interprets (3c) or (3b). Therefore we examined with care the possibility that the results could actually obey (4) despite the negative answer of the χ^2 test. If the ratios $V/[I^-]$ at constant $[H^+]$ and $[H_3AsO_4]$ are plotted against $[I^-]$, straight lines are obtained (runs 9-12, 23, 31, 32, 34, 37, and 39 of Table I) as is shown for $[H^+] = 0.05 M$ in Figure 1. If (4) were obeyed, a curve approaching a superior limit should be obtained. Finally if the values of

$$\frac{[H^+]^2 [H_3AsO_4] [I^-]^2}{V - k_1 [H^+] [H_3AsO_4] [I^-]} = \frac{1}{k_2} + \frac{k_3}{k_2} [I^-]$$

are plotted against $[I^-]$, choosing for k_1 the value which gives the best fit for (4), the points can be compared with the straight line defined by the values of k_2 and k_3 . They definitely show systematic negative deviations at low and high $[I^-]$ and systematic positive

(17) R. Deltheil, "Erreurs et Moindres Carrés," Gauthier Villars, Paris, 1930, p 108.

(18) M. R. Spiegel, "Statistics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 190.

deviations at intermediate $[I^-]$. Instead they are distributed randomly around the curve which can be calculated applying (3b) (which gives about the same value for k_1). We conclude that with a probability of more than 99.5% (3b) represents the actual mechanism of the main paths of the reaction, and (4) as well as (3a), (3d), and (3e) can be ruled out. The standard deviation, s , calculated from (3b) is 6.9%, which is not far from the predicted experimental error. However minor paths of order zero and three with respect to H^+ are not ruled out and actually are strongly suggested by the results. Using the weight equations¹⁷ we have calculated the standard deviations of the parameters of (3b) which are given in the text.

An analogous treatment was applied to the data of Table II with generally similar results. In particular (3b) is confirmed to be significantly superior to (3a) and (3d) and (3e) give a negative meaningless value for the rate constant corresponding to $(p,r) = (1,2)$. No definite conclusion can be reached from these runs about the relative merits of (3b) and (4) due to the narrow range of $[I^-]$. The purpose of these runs was in fact to rule out, even at $I = 3.00 M$, the contribution of a path first order with respect to H^+ and second order with respect to I^- . This contribution can be ruled out with a probability of more than 97.5% ($\chi^2_{(3b)} = 17.6$ and $\chi^2_{(3a)} = 30.1$; for 16 degrees of freedom $\chi^2_{(90\%)} = 23.5$ and $\chi^2_{(97.5\%)} = 28.8$).

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The Homogeneous Ruthenium-Catalyzed Reduction of Nitrobenzene

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Dodecacarbonyltriruthenium, pentacarbonylruthenium, and tris(acetylacetonato)ruthenium(III) were found to promote the homogeneous reduction of nitrobenzene to aniline by carbon monoxide and hydrogen in good yields and conversions. At $CO:H_2$ ratios higher than 1, diphenylurea is also a product of the reaction and its yields increase gradually with the $CO:H_2$ ratio. Product balance at very high $CO:H_2$ ratios shows that carbon monoxide participates in the reduction and thus the stoichiometry of the reaction is probably $C_6H_5NO_2 + 2CO + H_2 \rightarrow C_6H_5NH_2 + 2CO_2$. A reaction mechanism is proposed in which a phenylnitrene intermediate stabilized by bonding to ruthenium in a binuclear complex undergoes either hydrogenolysis to give aniline or CO insertion and hydrogenolysis to give 2,2'-diphenylurea. Pentacarbonyliron is considerably less active than ruthenium in promoting the reduction of nitrobenzene; a possible interpretation of this fact is given.

Introduction

There are several advantages in studying the reduction of nitrobenzene by carbon monoxide and hydrogen catalyzed by soluble metal complexes. Nitrobenzene, an industrially important chemical, has been more often reduced with hydrogen on heterogeneous catalysts and no really homogeneous catalytic systems have been reported in detail. Besides that, rather simple organic materials easily recognizable by the usual physical-chemical methods were anticipated to arise from its reduction.

Nitrobenzene had been reduced before by making use of metal-carbonyl systems. Formation of aniline from nitrobenzene has been briefly mentioned apparently with carbon monoxide and hydrogen in the presence of octacarbonyldicobalt.² Although yields were not specified, this reaction was assumed by us to occur under catalytic conditions. Aniline was also obtained³ from nitrobenzene in the presence of alkaline solutions presumably containing the $FeH(CO)_4^-$ anion. The latter system is substantially stoichiometric since the moles of

nitrobenzene reduced correspond to or are only slightly more than the moles of pentacarbonyliron introduced in the reaction. Nitrobenzene was also reduced stoichiometrically by $Fe(CO)_5$ under ultraviolet or γ -ray irradiation to give nitrosobenzene.⁴ The latter was isolated as monomeric and dimeric $Fe(CO)_3$ complexes. In view of the paucity of data available, it was interesting to see whether other metal carbonyls would catalyze the reduction of nitrobenzene to aniline.

The main prerequisites of a catalyst are that (a) it should not react in an irreversible way with the substrate, (b) it should provide a low-energy path for the formation of the intermediates, and (c) the intermediates should not be kinetically too stable. Ruthenium and osmium carbonyls appeared to satisfy the first requirement in view of their stability to oxidizing agents⁵ in general and to nitrobenzene in particular. Further, formation of aniline from nitrobenzene in the presence of metal carbonyls as catalysts may involve reduction either by hydrogen exclusively or by carbon monoxide and hydrogen. The possibility that the first steps of

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