J. Phys. Chem. 1988, 92, 4831-4835

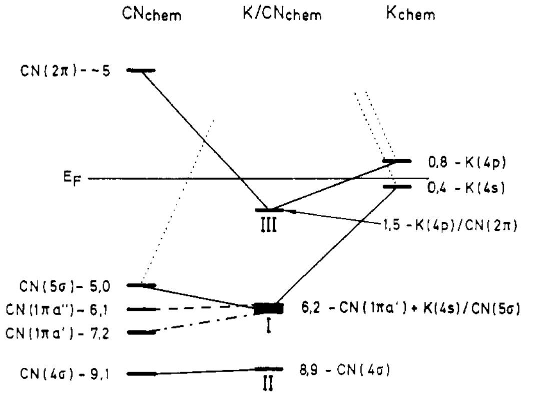

Figure 3. Correlation diagram for the 840 K phase of KCN derived from experimental data for chemisorbed K and CN. The binding energies (in eV) and orbital assignments are given in the figure. The dotted lines represent the antibonding levels, the solid, dashed, and dot/dashed the bonding orbitals. The data for CN_{chem} are taken from ref 19.

and the K is bonded to the C atom. Since the bonding combination of the orbitals is shifted to lower energy (higher binding energy) compared to the separated species, and the nonbonding orbitals are expected to remain essentially unshifted, we conclude that (1) the peak at 8.9 eV is due to the CN(4σ) orbital (on the N) as it does not participate in the KCN bond, and (2) the only K level with major contributions to the bond is the K(4s). Due to orbital symmetry, the interaction of the K(4s) with the CN(π) orbitals will be minor. We can therefore assign the CN(1π) orbitals, largely unaffected by the K–CN bond, to the feature at 6.2 eV.

The main contribution to the KCN bond arises from the bonding combination of the CN(5σ) and the K(4s) orbitals, which leads to a large chemical shift to higher binding energy, as indicated in Figure 3. The mixed orbital must be degenerate with the π orbitals within the resolution of the measurements. This assignment is strengthened by the intensity of the 6.2-eV feature, which is independent of photon energy.[15]

The level at 1.5 eV cannot be due to the antibonding combination of the K(4s) + CN(5σ) because the 4s level of metallic K is close to E_F.[10] On the basis of the calculation by Wimmer[20] which places the K(4p) level at 0.8 eV above E_F, the 1.5-eV peak is assigned to a bonding combination of the K(4p) + CN(2π) orbitals.

From inspection of the diagram in Figure 3 it is clear that more than eight valence electrons are necessary to fill the orbitals resulting from the KCN bond. We conclude that the KCN bond is indeed mostly covalent; however, the whole KCN molecule has a net negative charge. This implies that the chemisorption bond between the metal and $(KCN)^{\delta-}$ is predominantly due to the image charge interaction. The thermal stability of the chemisorbed KCN supports this conclusion.

In summary, PIES and HREELS data show that ionic KCN forms from the dissociative coadsorption of C_2N_2 and K in layers that are not directly in contact with the Pd(100) surface. The valence level emission features measured with PIES are in excellent agreement with UPS spectra of CN^- in NaCN(100).[14] The CN^- derived orbitals are measured at 7.4, 8.7, and 10.7 eV binding energy, corresponding to the 5σ, 1π, and 4σ MO's. HREELS of this phase show a surface mode due to bulk KCN and a CN stretching frequency of 256 meV. Upon heating to ~800 K, a new species of KCN, with PIES features at 1.5, 6.2, and 8.9 eV binding energy and vibrational losses at 17 and 232 meV, is observed. This species is identified as covalently bonded KCN, where the reduced ionicity of the KCN is due to the interaction of the KCN with the metal.

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High-Amplitude Hydrogen Ion Concentration Oscillation in the Iodate–Thiosulfate–Sulfite System under Closed Conditions

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In the closed system of iodate, hydrogen sulfite, and thiosulfate, high-amplitude, greatly damped pH oscillation occurs in unusually narrow concentration ranges of reactants. A semiquantitative description of the kinetic curves has been made in terms of the empirical rate laws of the subsystems by making allowance for cross effects. The skeleton model is closely related to the Lotka model, the archetype of chemical oscillators. A possible mechanism is suggested to give an account of experimental findings.

Introduction

In the abundant literature of oscillatory reactions there are very few results concerning the periodic change of pH. This is because most of the reactions exhibiting oscillatory kinetics occur in fairly acidic medium. There are only three reported pH oscillations in closed systems[1-3] and in each case the pH changes hardly exceed the experimental error. Recently high-amplitude pH oscillations were observed[4-9] for different systems in a continuously fed stirred

TABLE I: High-Amplitude pH Oscillations in CSTR

system	$\Delta[H^+]/M$	ΔpH	ref
$S^{2-} + H_2O_2$	10^{-6}	2.2	4
$ClO_2^- + S_2O_3^{2-}$	10^{-4}	0.13	5
$IO_3^- + HSO_3^- + Fe(CN)_6^{4-}$	5×10^{-4}	4.2	6
$IO_3^- + HSO_3^-$ + thiourea	5×10^{-4}	3.8	7
$IO_3^- + HSO_3^- + S_2O_3^{2-}$	5×10^{-4}	4.5	8
$S_2O_3^{2-} + H_2O_2$	10^{-5}	3.5	9

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TABLE II: The Number of Extrema as a Function of Excess IO_3^- [a]

$10^3[IO_3^-]$/M	no. of extrema	R	$10^3[IO_3^-]$/M	no. of extrema	R
0.005	1	0.606	0.1025	5	1.52
0.0075	1	0.909	0.014	5	1.70
0.009	1	1.09	0.015	5	1.82
0.0095	3	1.15	0.0175	5	2.12
0.010	7	1.21	0.020	3	2.42
0.011	5	1.33	0.025	3	3.03

[a] Initial concentrations: $[Na_2S_2O_3]_0 = 0.0105$ M; $[Na_2SO_3]_0 = 0.0195$ M; $[H_2SO_4]_0 = 0.005$ M. $R = [IO_3^-]_0/[([SO_3^{2-}]_0/3) + ([S_2O_3^{2-}]/6)]$.

tank reactor (CSTR) (Table I).

We observed recently an extremely sharp minimum in pH for the closed system of iodate–thiosulfate–hydrogen sulfite, while in a CSTR high-amplitude oscillation in hydrogen ion concentration was found.[8] A semiquantitative description of the kinetics in both the closed and open systems could be given in terms of the overall empirical rate equations of the subsystems, taking into account the catalytic effect of thiosulfate on iodate oxidation of hydrogen sulfite, and the inhibitory effect of hydrogen sulfite on iodate oxidation of thiosulfate, as well as the equilibrium between sulfite and hydrogen sulfite ions.

Additional experiments revealed that a high-amplitude, damped oscillatory change of pH occurs even in the closed system of IO_3^-–$S_2O_3^{2-}$–HSO_3^- in certain rather narrow concentration ranges of the reactants.

Experimental Section

All chemicals were of analytical quality and used as received. Stock solutions of KIO_3, Na_2SO_3, $Na_2S_2O_3$, and H_2SO_4 were made by using doubly distilled, deoxygenated water. Sulfite solutions were made daily and kept under nitrogen to prevent the autoxidation. The concentrations of sulfite and thiosulfate solutions were checked iodometrically.

pH measurements were made with a Radelkis OP 208 pH meter and a combined glass electrode. For standardization a potassium hydrogen phthalate buffer was used.

All reactions were carried out in a 50-mL thermostated glass vessel. To avoid acidic decomposition of thiosulfate, appropriate volumes of sulfuric acid and sulfite solutions were first mixed, then thiosulfate solution was added, and the reaction was started by adding the iodate solution. The reaction mixture was stirred with a magnetic stirrer. Stirring speed has no effect on the pH vs time curves.

Results

More than one extremum in the pH vs time curves appears but only if the ratios of concentrations of the reactants are within certain limits. The reproducibility of the experiments is good; however, the concentrations of the reactants have to be adjusted with care since the concentration ranges where oscillatory kinetics is observed are unusually narrow. Figure 1 and Table II show that exotic behavior, that is, more than one extremum on the kinetic curves, occurs only if iodate is in excess corresponding to the stoichiometry of reactions 1 and 2, that is, when $R = [IO_3^-]_0/([HSO_3^-]_0/3 + [S_2O_3^{2-}]_0/6)$ exceeds one. The maximum number of extrema, corresponding to three periods of a greatly damped oscillation, occurs in an extremely narrow range of R. If the initial concentration of iodate is less than necessary for the oxidation of hydrogen sulfite, the pH monotonously decreases until the total amount of iodate is consumed (curve e).

$$IO_3^- + 3HSO_3^- = I^- + 3SO_4^{2-} + 3H^+ \qquad (1)$$

$$IO_3^- + 6S_2O_3^{2-} + 6H^+ = I^- + 3S_4O_6^{2-} + 3H_2O \qquad (2)$$

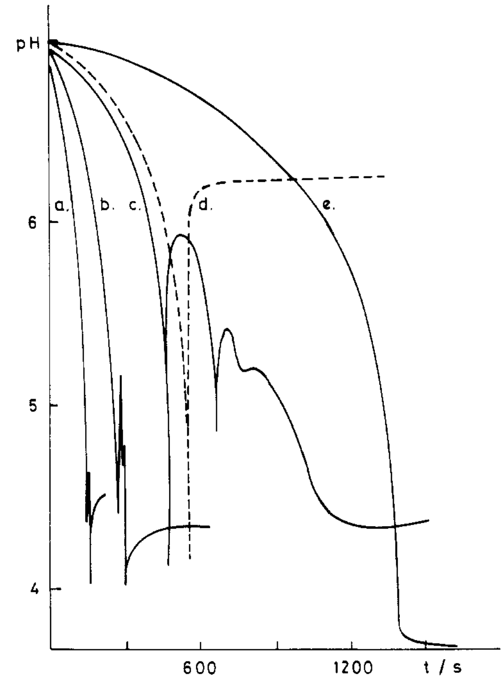

Figure 1. Experimental pH vs time curves at different initial iodate concentrations (M) $[SO_3^{2-}]_0 = 0.0195$, $[H^+]_0 = 2[H_2SO_4]_0 = 0.010$, $[S_2O_3^{2-}]_0 = 0.0105$, $[IO_3^-]_0 = 0.025$ (a); 0.015 (b); 0.010 (c); 0.008 (d); 0.005 (e); $T = 25$ °C.

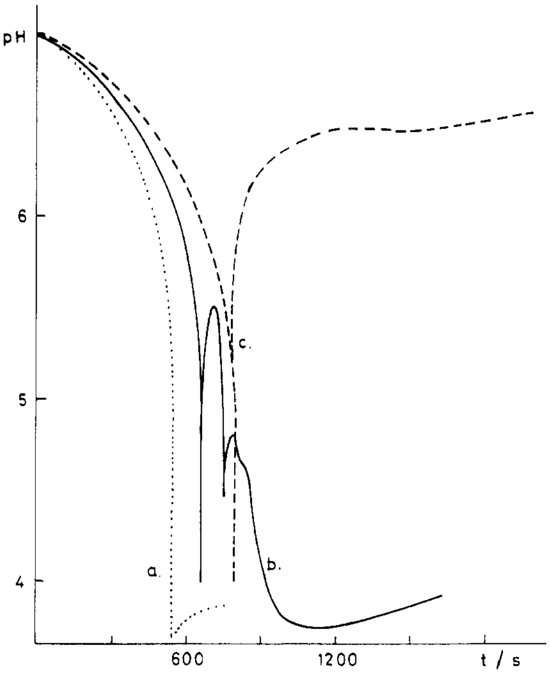

Figure 2. The effect of initial hydrogen ion concentration on the kinetic curves: $[IO_3^-]_0 = 0.010$, $[SO_3^{2-}]_0 = 0.020$, $[S_2O_3^{2-}]_0 = 0.010$, $[H^+]_0 = 2[H_2SO_4]_0 = 0.0098$ (a); 0.0092 (b); 0.0088 (c); $T = 25$ °C.

The ratio of the initial concentrations of free acid to thiosulfate is of crucial importance. Oscillations occur if the initial concentration of free acid added in the form of sulfuric acid is slightly less than the initial concentration of thiosulfate. Figure 2 shows that oscillatory behavior is observed when $1.1 \times 2[H_2SO_4]_0 > [S_2O_3^{2-}]_0 > 1.05 \times 2[H_2SO_4]_0$. If the excess of thiosulfate is bigger, a single sharp minimum occurs, while if the excess of

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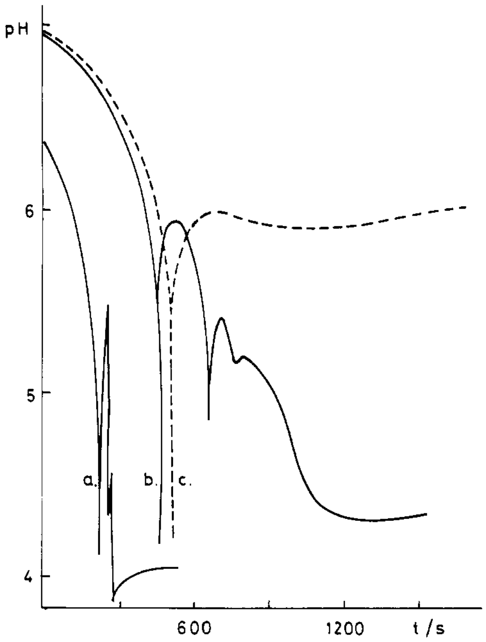

Figure 3. pH vs time curves at different sulfite concentrations (M) in the iodate–sulfite–thiosulfate system: $[IO_3^-]_0 = 0.010$, $[S_2O_3^{2-}]_0 = 0.0105$, $[H^+]_0 = 2[H_2SO_4]_0 = 0.01$, $[SO_3^{2-}]_0 = 0.015$ (a); 0.0195 (b); 0.0205 (c); $T = 25$ °C.

thiosulfate is smaller, or even if sulfuric acid is in excess, the oxidation of sulfite and thiosulfate is followed by the iodate–iodide reaction.

The ratio of the initial concentrations of hydrogen sulfite and thiosulfate is also important. As shown in Figure 3 the shape of the kinetic curves and the character of the reaction greatly changes by decreasing sulfite concentration at constant concentrations of thiosulfate and sulfuric acid. Over a certain limit a single minimum occurs. In the absence of sulfite no exotic behavior was observed. The importance of this fact will be discussed later.

In contrast with the open system, temperature has no significant effect on the kinetic characteristics in the closed system. Practically the same behavior was observed in the 20–50 °C interval.

Discussion

The System of Empirical Rate Equations. In the study of oligooscillatory reactions we could quantitatively or semiquantitatively describe the complex kinetic behavior in terms of the empirical rate laws of the subsystems and certain additional terms expressing the interactions between the subsystems.[10-12] The same approach was applied in the case of an oscillatory system in a CSTR.[13] In the present case the two subsystems are the iodate–hydrogen sulfite and the iodate–thiosulfate reactions. Their stoichiometries are given by eq 1 and 2, while the rate equations are as follows:[8,14-16]

$$v_1 = -\frac{d[IO_3^-]}{dt} = k_1[IO_3^-][HSO_3^-][H^+] + k_1'[IO_3^-][HSO_3^-]^2 \qquad (1')$$

$$v_2 = -\frac{d[IO_3^-]}{dt} = k_2[IO_3^-][S_2O_3^{2-}]^2[H^+]^2 \qquad (2')$$

Previously we found[8] that iodate oxidation of sulfite is catalyzed by thiosulfate, while iodate oxidation of thiosulfate is inhibited by sulfite; that is, the rates when a mixture of hydrogen sulfite and thiosulfate is oxidized by iodate should be written as follows:

$$v_1 = k_1[IO_3^-][HSO_3^-][H^+] + k_1'[IO_3^-][HSO_3^-]^2 + k_c[IO_3^-][HSO_3^-][S_2O_3^{2-}][H^+]^2 \qquad (1'')$$

$$v_2 = k_2[IO_3^-][S_2O_3^{2-}]^2[H^+]^2/(1 + k_i[HSO_3^-]) \qquad (2'')$$

To describe the oscillatory change of pH in CSTR it is not necessary to assume any other chemical reaction. However, in a closed system, not more than one extremum can occur unless some other reaction takes place. The most likely candidate for this reaction is the oxidation of thiosulfate to sulfate, which in contrast with the oxidation of thiosulfate to tetrathionate, results in an increase of hydrogen ion concentration. Since sulfate is formed when thiosulfate is oxidized by an excess of iodate, but tetrathionate is oxidized by iodate very slowly, tetrathionate is not an intermediate in the route leading to the formation of sulfate. The situation is similar to the oxidation of thiosulfate by chlorite.[17]

It seems most likely that thiosulfate is partially oxidized to sulfite, which is then easily oxidized further to sulfate. The stoichiometry of the oxidation of thiosulfate by iodate to hydrogen sulfite is given by the following equation:

$$2IO_3^- + 3S_2O_3^{2-} + 3H_2O = 2I^- + 6HSO_3^- \qquad (3)$$

The formation of sulfite from thiosulfate is of crucial importance from the point of view of oscillatory behavior in a closed system since it results in a regeneration of sulfite, which then makes possible the repetition of the cycle.

The rate law of the oxidation of thiosulfate to hydrogen sulfite must give an account of the finding that when thiosulfate is in excess no formation of sulfate occurs; that is, thiosulfate acts as a self-inhibitor of its oxidation to sulfite. Without such an effect the calculation indicated oscillatory kinetics even when no hydrogen sulfite is initially present. However, oscillatory kinetics are found only when the initial concentrations of hydrogen sulfite and thiosulfate are comparable. An important condition of the pH oscillation is that the order of the hydrogen ion concentration must be lower than that in the competing reaction (2). This relation makes possible the formation of hydrogen sulfite according to reaction 3 at relatively small hydrogen ion concentration. All results suggest the following rate law for reaction 3

$$v_3 = -\frac{d[IO_3^-]}{dt} = k_3[IO_3^-][S_2O_3^{2-}][H^+]/(1 + k_i[HSO_3^-] + k_i'[S_2O_3^{2-}][H^+]) \qquad (3')$$

We found that the rate of reaction 1, under the conditions where oscillatory behavior occurs, is better described by a further catalytic term expressing the strong hydrogen ion dependence of the catalytic effect of thiosulfate:

$$v_1 = [IO_3^-](k_1[HSO_3^-][H^+] + k_1'[HSO_3^-]^2 + k_c[HSO_3^-] \times [S_2O_3^{2-}][H^+]^2 + k_c'[HSO_3^-][S_2O_3^{2-}][H^+]^3) \qquad (1''')$$

For a quantitative description, the consideration of the acidic character acid–base equilibrium

$$SO_3^{2-} + H^+ \rightleftharpoons HSO_3^- \qquad (4)$$

is obviously necessary. In the calculations by a semiimplicit Runge–Kutta method the equilibrium was taken into consideration by the rate laws:

$$v_4 = k_4[SO_3^{2-}][H^+] \qquad (4')$$

$$v_{-4} = k_{-4}[HSO_3^-] \qquad (-4')$$

The calculations based on stoichiometric eq 1–4 and rate laws (1‴), (2″), (3′), (4′), and (−4′) well describe all the characteristic

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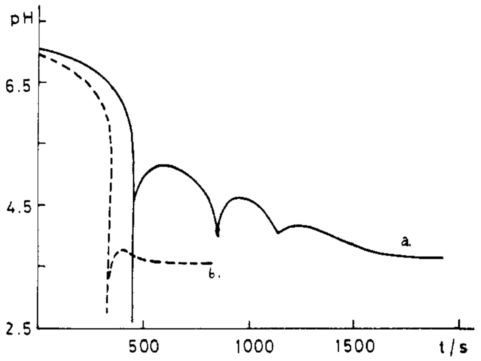

Figure 4. Calculated oscillatory curve. The calculation was carried out on the basis of (1)–(4) stoichiometric and (1‴), (2″), (3′), (4′), and (−4′) rate equations by using rate constants as follows: $k_1 = 8800$ $M^{-2}\ s^{-1}$; $k_1' = 11$ $M^{-2}\ s^{-1}$; $k_c = 1 \times 10^{11}$ $M^{-4}\ s^{-1}$; $k_c' = 5 \times 10^{16}$ $M^{-5}\ s^{-1}$; $k_2 = 6 \times 10^{11}$ $M^{-4}\ s^{-1}$; $k_3 = 2 \times 10^5$ $M^{-2}\ s^{-1}$; $k_4 = 5 \times 10^{10}$ $M^{-1}\ s^{-1}$; $k_{-4} = 3 \times 10^3$ s^{-1}; $k_i = 5 \times 10^4$ M^{-1}; $k_i' = 2 \times 10^9$ M^{-2}. The initial concentrations (M) are $[IO_3^-]_0 = 0.01$, $[S_2O_3^{2-}]_0 = 0.01$, $[H^+]_0 = 2[H_2SO_4]_0 = 0.0092$, $[SO_3^{2-}]_0 = 0.02$. In the case of curve b $[H^+]_0 = 0.01$ M.

features found experimentally. These are as follows: (i) the number of extrema; (ii) the strong damping; (iii) the lack of oscillation when no hydrogen sulfite is initially present; (iv) the extreme sensitivity to the ratio of the initially added amounts of thiosulfate and free acid.

Curve a of Figure 4 shows a typical oscillatory curve. The first pH minimum is lower than the experimentally found value. This is, at least partly, due to the slow response of the pH electrode.[8] The period times are slightly greater than that found experimentally. Curve b shows that in accordance with the experiment, there is no oscillatory behavior when the initial amounts of thiosulfate and free acid are equal. However, the calculations show oscillation until the ratio of the initial amount of thiosulfate and free acid decreased to 0.5, while according to the experiments no oscillatory kinetics occurs below 0.9.

By extending the system of differential equations with the flow terms, the oscillatory change of pH observed in a CSTR can be well described. There is practically no difference between this treatment and the previous one[8] which did not consider the regeneration of hydrogen sulfite by reaction 3. This agreement indicates that in the open system reaction 3 is of minor importance compared to the supply of hydrogen sulfite by the flow.

There are two obvious tasks: first, to simplify the system of differential equations to find the minimum requirements for oscillatory behavior by using *arbitrary* rate constants but retaining the basic mechanistic features, and second, to explore the very complex chemical background of the observed phenomena which then later may provide a more quantitative description of the results.

Modelling of the Oscillatory Reaction. Obviously, one can disregard the dissociation of HSO_3^-. As a matter of course, if hydrogen sulfite was to completely dissociate, no exotic behavior could be found: there would not be any change in the hydrogen ion concentration during the reaction. The stoichiometry given by eq 1–3 is not important and a skeleton of the elementary reactions can be given as follows:

$$A + B \rightarrow Y \tag{S1}$$

$$A + B + X \rightarrow P_1 \tag{S2}$$

$$A + Y + X \rightarrow 2X + P_2 \tag{S3}$$

In this skeleton model A *corresponds* to (but does not stand for!) iodate, B to thiosulfate, Y to hydrogen sulfite, X to hydrogen ion, P_1 to tetrathionate, and P_2 to sulfate.

Numerical solution of the corresponding rate equations using suitably chosen parameters gives oscillatory change for concentrations of X and Y. Figure 5 shows that the oscillation is greatly damped. The basis of the oscillatory behavior is the *alternation* of the autocatalytic formation (S3), and the first-order consumption (S2), of X and the formation of Y in (S1). *Alternator* presents itself as a name for this type of chemical oscillator. It is closely related to the original Lotka model which consists of the following three elementary reactions:

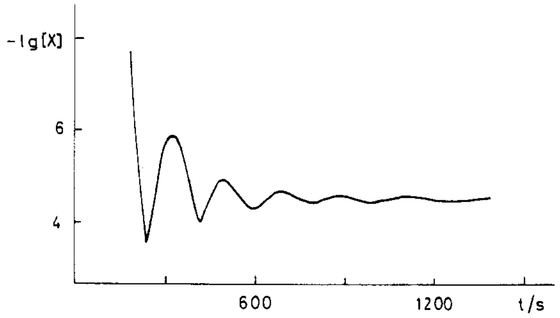

Figure 5. Oscillatory curve calculated on the basis of simplified model (S1)–(S3): $k_{S1} = 0.1$ $M^{-1}\ s^{-1}$; $k_{S2} = 1 \times 10^4$ $M^{-2}\ s^{-1}$; $k_{S3} = 1 \times 10^5$ $M^{-2}\ s^{-1}$; $[X]_0 = 1 \times 10^{-7}$ M; $[Y]_0 = 1 \times 10^{-3}$ M; $[A]_0 = 0.01$ M; $[B]_0 = 0.01$ M.

$$A \rightarrow Y \tag{S4}$$

$$X \rightarrow P \tag{S5}$$

$$Y + X \rightarrow 2X \tag{S6}$$

Both the similarities and differences are evident by the comparison of the two models. The *alternator* is nearer to the chemical reality since it expresses that the reactions of the same reactant give different products, and since (S6), although provides the mathematical condition of the oscillatory characteristics, chemically cannot occur in this form. We believe, however, that the oscillatory reaction found in the iodate–thiosulfate–sulfite system is the most closely related to the original Lotka model among all the known chemical oscillators, and that the *alternator* helps us to understand the chemical basis of such an oscillatory reaction. Furthermore, the *alternator* may lead to the discovery of other oscillatory reactions of this type. The damped nature of the oscillation is an inherent consequence of the *alternator*; however, the fact that at most three periods could be found is due to the parameters of the given system.

Although the number of the observed extrema is very limited, this system is an oscillatory and not an oligooscillatory one. In case of an oligooscillatory system, by changing the parameters one cannot exceed a small limiting value of extrema, and this is certainly not the case with the system in question.

Mechanistic Considerations. A set of elementary and quasi-elementary reactions can be given from which the empirical rate equations can be derived by appropriate simplifications.

The first term of the "empirical" rate law (1‴) follows from the preequilibrium (M1) and the subsequent relatively slow step (M2), while the second term reflects the (M1) preequilibrium and the (M3) quasi-elementary reactions:

$$IO_3^- + HSO_3^- \rightleftharpoons IO_3HSO_3^{2-} \tag{M1}$$

$$IO_3HSO_3^{2-} + H^+ \rightarrow SO_4^{2-} + IO_2^- + 2H^+ \tag{M2}$$

$$IO_3HSO_3^{2-} + HSO_3^- \rightarrow 2SO_4^{2-} + IO^- + 2H^+ \tag{M3}$$

This latter reaction most likely consists of two steps:

$$IO_3HSO_3^{2-} + HSO_3^- \rightarrow IO_2HSO_3^{2-} + SO_4^{2-} + H^+ \tag{M3a}$$

$$IO_2HSO_3^{2-} \rightarrow IO^- + SO_4^{2-} + H^+ \tag{M3b}$$

The oxidation of thiosulfate to hydrogen sulfite occurs via the preequilibrium (M4) and the quasi-elementary reaction (M5) which, similarly to (M3), occurs in several steps:

$$IO_3^- + H^+ + S_2O_3^{2-} \rightleftharpoons IO_3HS_2O_3^{2-} \tag{M4}$$

$$IO_3HS_2O_3^{2-} + H_2O \rightarrow IO^- + 2HSO_3^- + H^+ \tag{M5}$$

The competing oxidation of thiosulfate to tetrathionate is described by the preequilibria (M4) and (M6) and the subsequent relatively slow (M7):

$$IO_3HS_2O_3^{2-} + H^+ \rightleftharpoons IO_3H_2S_2O_3^- \qquad (M6)$$

$$IO_3H_2S_2O_3^- + S_2O_3^{2-} \rightarrow IO_2^- + S_4O_6^{2-} + H_2O \qquad (M7)$$

The consideration of the second preequilibrium is made necessary by the finding that, in the route leading to tetrathionate, the concentrations of both thiosulfate and the hydrogen ion are on the second power.

The catalytic effect of thiosulfate on the oxidation of hydrogen sulfite is explained by (M8) and (M9)

$$IO_3H_2S_2O_3^- + HSO_3^- \rightarrow SO_4^{2-} + S_2O_3^{2-} + IO_2^- + 3H^+ \qquad (M8)$$

$$IO_3H_2S_2O_3 + HSO_3^- + H^+ \rightarrow SO_4^{2-} + S_2O_3^{2-} + IO_2^- + 4H^+ \qquad (M9)$$

These reactions, together with the preequilibria (M4) and (M6), are responsible for the third and the fourth terms of the rate law (1‴), resp. In this set of elementary steps, (M8) is responsible for the inhibition effect of hydrogen sulfite in the oxidation of thiosulfate, that is, for the $k_i[HSO_3^-]$ term in the denominator of rate laws (2″) and (3′). In principle, a similar inhibition effect was due to (M9). According to the experiments, however, its weight is negligible. However, due to the obvious differences in the catalytic and inhibition effects, the catalytic effect due to (M9) appears to be significant and therefore even the fourth term in (1‴) should have been considered.

The finding that with increasing hydrogen ion concentration, and in an excess of thiosulfate, the oxidation of thiosulfate to hydrogen sulfite is suppressed in comparison with the competing oxidation to tetrathionate can be explained by (M6) and (M7). These steps can be responsible for the $k_i'[S_2O_3^{2-}][H^+]$ term in the denominator of (3′).

Of course, a great number of further reactions must occur involving iodite and hypoiodite. There are good reasons to assume that these reactions are rather complex and involve the formation of adducts between the reactants. These fast reactions, however, probably are of secondary importance in the dynamics of the system.

It goes without saying that reactions M1–M9 do not represent *the* mechanism of the reaction. However, it seems that it is the simplest and chemically plausible set of elementary and quasi-elementary reactions which may be responsible for the observed phenomena.

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Dissociation Energy of an Isolated Triplet Acetone Molecule

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Fluorescence lifetime measurements of acetone in a seeded supersonic molecular beam reveal a sharp increase in the decay rate at an excitation energy of about 32 700 cm^{-1}. There is a concomitant sharp decrease in the emission intensity. It is suggested that these changes are due to the onset of the homolytic dissociation of acetone to methyl and acetyl radicals. The barrier for this reaction on the triplet T_1 surface is determined to be at 32 700 ± 50 cm^{-1} above the ground state.

Introduction

The gas-phase photodissociation of acetone involves the primary reaction

$$CH_3COCH_3 \rightarrow CH_3CO + CH_3 \qquad \Delta H^\circ_{298} = 81 \text{ kcal/mol} \qquad (1)$$

It is believed to take place on the triplet nπ^* surface. Previous estimates of the energy barrier corresponding to this reaction ranged between 6 and 17 kcal/mol.[1-4] Table I summarizes these results and the experimental techniques used in obtaining them. All previous work was done at ambient temperatures, making it necessary to correct for the initial energy distribution of the molecules. Furthermore, since relatively high-pressure conditions were used, extrapolation to zero pressure was required in some cases.

We report a measurement of the dissociation energy on the triplet energy surface, taken in a supersonic seeded molecular beam. Under these conditions, the molecules are both cold and isolated from collisions, allowing an almost direct measurement. Our result is 32 700 ± 50 cm^{-1}, corresponding to 93.4 kcal/mol above the ground state. Assuming that the T_1 surface is at 80 kcal/mol, this value corresponds to a barrier of 13.4 kcal/mol.

TABLE I: Previous Estimates of the Barrier to Reaction 1

method	energy barrier, kcal/mol	ref
1. kinetic analysis of photolysis experiments	6.4	1
2. kinetic analysis using RRK theory	10.3	2
3. photosensitization of biacetyl	15.0	3
4. low-pressure bulk phosphorescence	11.5[a]	4

[a] Assuming that the triplet zero point energy of the triplet is 80 kcal/mol above S_0.

Experimental Section

The pulsed supersonic beam source was described earlier.[5] Acetone was seeded in helium and expanded through an orifice into a vacuum chamber maintained at 10^{-7} Torr. Orifice diameters used were 0.03 and 0.3 mm. The expanding jet was intersected by a tunable dye laser beam about 20–50 nozzle diameters downstream. The resulting fluorescence was observed at right angles, through a 370-nm cutoff filter. The laser was either an excimer laser pumped dye laser (Lambda Physik, 0.2 cm^{-1}

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