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A Kinetic Investigation of the Insertion of Ketones into the Dioxygen Adduct $Pt(PPh_3)_2O_2$

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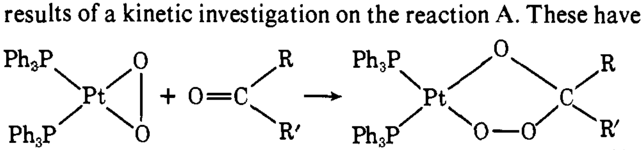
Abstract: The kinetics of the insertion reaction A have been studied with different ketones in different solvents. The experimental rate equation is in agreement with a dual pathway reaction mechanism. The major pathway involves precoordination of the ketone to the vacant axial coordination site of platinum followed by insertion. The minor pathway requires a prior activation of the dioxygen moiety. The nature of the transition states and the activated form of the dioxygen complex are discussed by means of an analysis of the activation parameters and solvent effects.

The synthesis and reactivity of dioxygen complexes with low oxidation state transition metal complexes have been investigated in recent years[1] since they could be related to the mechanisms of catalytic activation of dioxygen both on surfaces and in metal enzymes.[2] One interesting reaction involves the insertion into $Pt(PPh_3)_2O_2$ of an unsaturated group such as the carbonyl group of some organic molecules[3,4] or the double bond of activated olefins.[5] Such an insertion reaction can be considered to be a model for some of the important steps of catalytic selective oxidation such as the heterogeneous epoxidation of ethylene[6] or a particular metal-catalyzed olefin oxidation.[7]

Although a qualitative mechanistic study of this sort of reaction has been reported,[5] a detailed kinetic study is required to substantiate any proposed mechanism. We now describe the results of a kinetic investigation on the reaction A. These have been reported in a preliminary way elsewhere.[8]



(A)

Experimental Section

Solvents and Reagents. $Pt(PPh_3)_2O_2$ was obtained as previously reported;[9] solvents were distilled and dried over sodium or calcium hydride; ketones, all purchased commercially, were carefully distilled before use and their purity was checked by VPC.

Kinetic Experiments. All kinetics runs were carried out under pseudo-first-order conditions with a 50-1000 times excess of ketone with respect to the platinum complex whose concentration in solution was about 10^{-3} M. The reactions were carried out in dry, degassed solvents and were followed by monitoring absorbance changes at about 340 nm as a function of time. Good first-order plots were always obtained for up to 80% or more reaction of the platinum complex. Representative first-order kinetic plots are shown in Figure 1, where $[PtO_2]_0$ and $[PtO_2]_t$ are concentrations of $Pt(PPh_3)_2O_2$ at time = 0 and any other time, t. The results of the kinetic measurements are given in Tables IS, IIS, and IIIS.

Results

Under the experimental conditions used the insertion reaction was found to be first order in the platinum complex for all the incoming ketones and in all the solvents investigated. Linear plots were obtained from plots of the pseudo-first-order constant, k_{obsd}, vs. different concentrations of the ketone (Figure 2). Such linear plots have a small intercept on the y axis, which is independent of the nature of the ketone. These data suggest the following experimental rate law:

$$\text{rate} = k_{obsd}[PtO_2] = (k_A + k_B[\text{Ket}])[PtO_2] \qquad (1)$$

where Ket = ketone, $PtO_2 = Pt\,(PPh_3)_2O_2$. This equation was found to be valid for a series of nondonor solvents such as benzene, chloroform, or 1,2-dichloroethane as well as a donor solvent such as dimethylformamide (DMF).

For solvent mixtures containing DMF and benzene, the donor solvent has been found to play an important role in the overall kinetics since both the values k_A and k_B of the experimental rate equation (1) are dependent on the concentration of the donor solvent. This is illustrated in Figure 3 for different mixtures of C_6H_6/DMF with acetone as the incoming ketone. By plotting $1/k_A$ and $1/k_B$ vs. the DMF concentration, linear plots are obtained (Figure 4) which are of the general form[10]

$$\begin{aligned} 1/k_A &= (1/\mathbf{a})(1 + \mathbf{a}'[\text{DMF}]) \\ 1/k_B &= (1/\mathbf{b})(1 + \mathbf{b}'[\text{DMF}]) \end{aligned} \qquad (2)$$

These can be incorporated in the experimental rate law to give

$$\text{rate} = \left(\frac{\mathbf{a}}{1 + \mathbf{a}'[\text{DMF}]} + \frac{\mathbf{b}}{1 + \mathbf{b}'[\text{DMF}]}[\text{Ket}]\right)[PtO_2] \quad (3)$$

The values of **a** and **b** from Figure 4 are $1.27 \times 10^{-4}\ \text{s}^{-1}$ and

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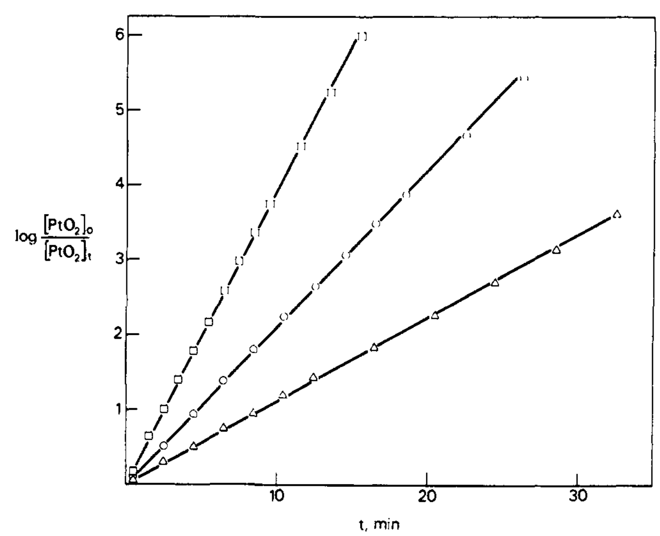


Figure 1. First-order plots in the platinum complex at various acetone concentrations in benzene solution at 30 ± 0.1 °C. $[(PPh_3)_2PtO_2] = (9.7 \pm 0.3)10^{-4}$ M. [acetone] (M) △, 0.22; ○, 0.44; □, 1.05.

$1.43 \times 10^{-3}\ s^{-1}\ mol^{-1}$ L, respectively, at 30 °C. These values are very similar to the values at 30 °C of k_A [$(1.27 \pm 0.18)10^{-4}\ s^{-1}$] and k_B [$(1.40 \pm 0.03)10^{-3}\ s^{-1}\ mol^{-1}$ L] obtained from Figure 2 using pure benzene. Moreover, also from Figure 4 both **a**′ and **b**′ have very similar values, 0.80 and 0.83 mol^{-1} L, respectively, at 30 °C. These results suggest that the experimental rate law can be rewritten as

$$\text{rate} = \frac{1}{1 + \mathbf{a}'[\text{DMF}]}(k_A + k_B[\text{Ket}])[\text{PtO}_2] \qquad (4)$$

In agreement with the above assumption we have obtained the rather satisfactory linear relationship with a nonzero intercept shown in Figure 5, by plotting $1/k_{obsd}$ vs. the DMF concentration for different acetone concentrations. This corresponds to an equation of the type

$$1/k_{obsd} = A + B[\text{DMF}] \qquad (5)$$

where $A = 1/(k_A + k_B[\text{Ket}])$ and $B = \mathbf{a}'/(k_A + k_B[\text{Ket}])$. The experimental rate law (eq 4) suggests the presence of two parallel mechanistic paths (A and B), which are shown in Figure 6. Assuming the steady-state approximation for the intermediates **1** and **2** and that the five-coordinate intermediate **3**, which exists only in a good donor solvent such as DMF, is an unreactive species, then the following rate law can be derived:

$$\text{rate} = \frac{1}{1 + K_{DMF}[\text{DMF}]}\left(\frac{k_3k_4[\text{Ket}]}{k_{-3} + k_4[\text{Ket}]} + \frac{k_1k_2[\text{Ket}]}{k_{-1} + k_2}\right)[\text{PtO}_2] \qquad (6)$$

If $k_4[\text{Ket}] \gg k_{-3}$ and $k_{-1} \gg k_2$, the rate law becomes

$$\text{rate} = \frac{1}{1 + K_{DMF}[\text{DMF}]}\left(k_3 + \frac{k_1}{k_{-1}}k_2[\text{Ket}]\right)[\text{PtO}_2] \qquad (7)$$

which is in perfect agreement with the experimental one if $K_{DMF} = \mathbf{a}'$, $k_3 = k_A$, and $(k_1/k_{-1})k_2 = k_B$.

Discussion

The existence of two parallel mechanisms for the reaction under investigation is not unexpected for a formally square-planar d^8 platinum(II) complex because nucleophilic substitutions at such complexes normally proceed via two parallel mechanisms.[11] As found for nucleophilic substitution reactions of platinum(II) complexes, the most important pathway is the preliminary coordination of the ketone, acting as a donor ligand, at the vacant coordination site of platinum (intermediate **1** in Figure 6). This coordination is followed by an insertion of the carbonyl group of the ketone into the PtO_2 moiety.

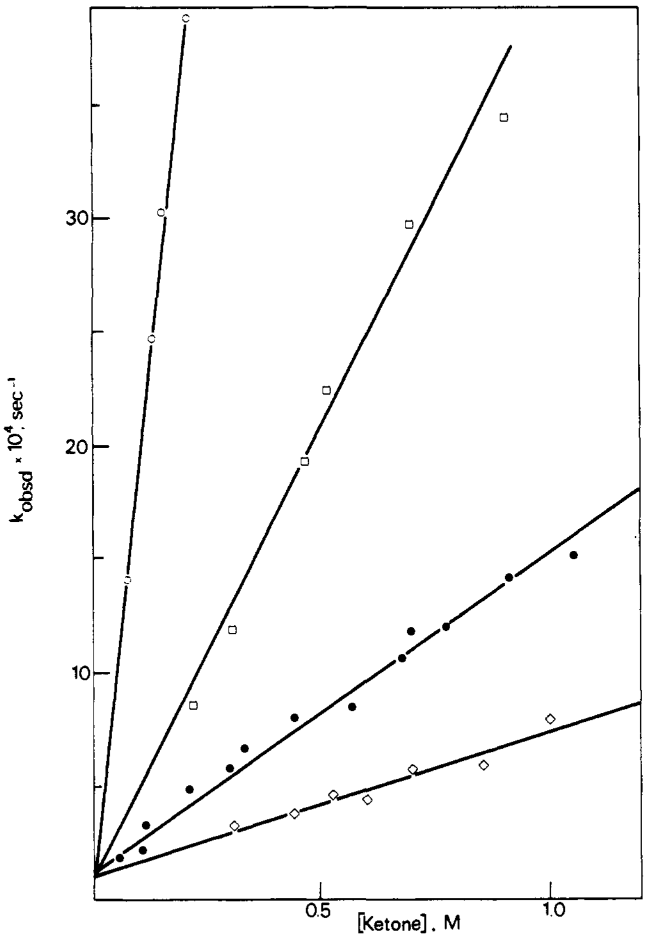


Figure 2. Plot of the observed pseudo-first-order rate constants vs. ketone concentration for different ketones in benzene solution at 30 ± 0.1 °C. $[(PPh_3)_2PtO_2] = (1.4 \pm 0.4)10^{-3}$ M; ○, cyclohexanone; □, cyclopentanone; ●, acetone; ◇, methyl ethyl ketone.

Direct external attack of the ketone, acting as an electrophile, on the metal coordinated dioxygen can be discarded by taking into account the following observations. The presence of a good donor solvent such as DMF successfully competes for the free coordination site of platinum and slows down the reaction. The reaction is also strongly dependent on steric effects. Whereas acetone and methyl ethyl ketone exhibit a comparable reactivity, a related and more hindered ketone such as *tert*-butyl methyl ketone does not react at all. Such a lack of reactivity must be governed by some severe steric hindrance in the coordination sphere of the metal involving the entering ketone and the triphenylphosphine ligands. Any external attack of the ketone on the metal coordinated O_2 species should not be so affected by steric effects. Finally, the rather negative values of $\Delta S^{\ddagger}$ found in at least three solvents of different basicity and dielectric constant (Table IV) are in complete agreement with bimolecular association.

The insertion may be regarded to be a nucleophilic attack of a metal-coordinated peroxide anion[12] into the carbon atom of the metal-coordinated carbonyl group of the ketone. This is a facile reaction probably because the electrophilic character of the carbon atom of the carbonyl group is enhanced by the coordination to the platinum center.[13] The order of reactivity that we have found (when steric effects are not too important) is in good agreement with that reported for reactions with other classical nucleophiles,[14,15] i.e., 1,1,1-trifluoroacetone ≫ ace-

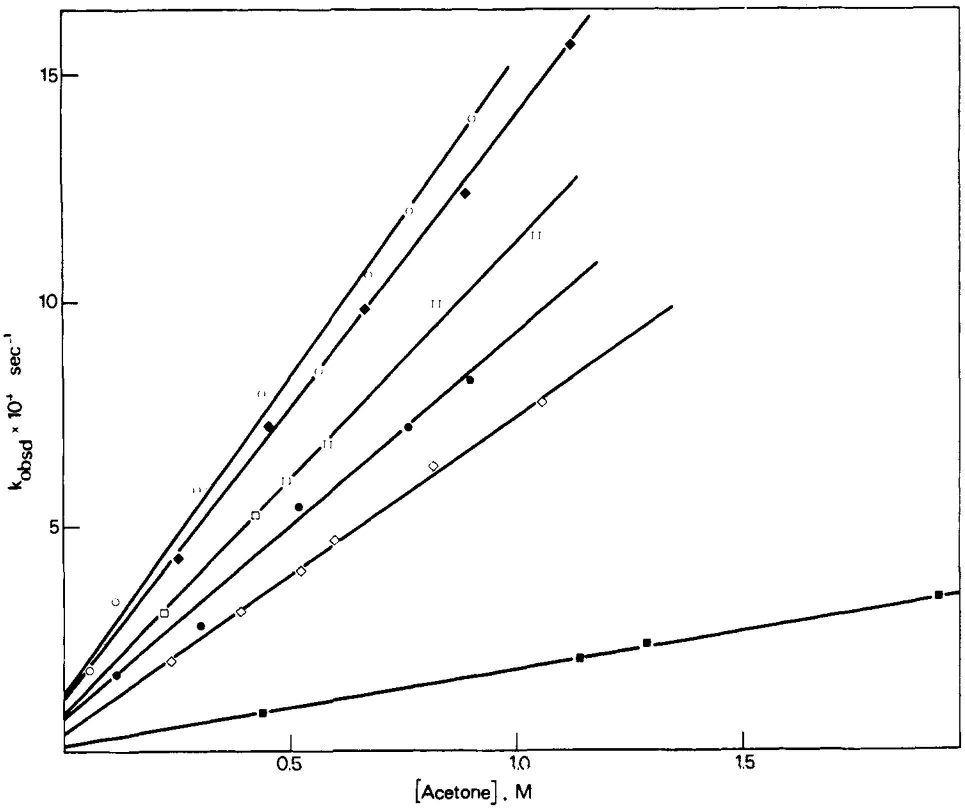


Figure 3. Plot of the observed pseudo-first-order rate constants vs. acetone concentration at various dimethylformamide concentrations in benzene at 30 ± 0.1 °C. [(PPh$_3$)$_2$PtO$_2$] = (1.4 ± 0.3)10^{-3} M; [DMF] (M) ○, none; ♦, 0.217; □, 0.425; ●, 0.845; ◇, 1.29; ■, 11.5.

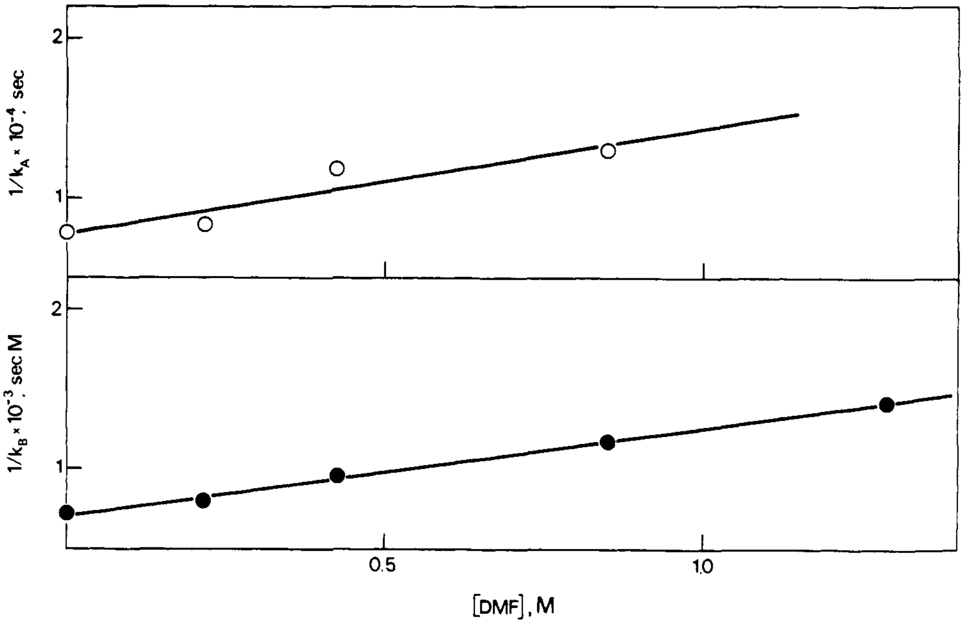
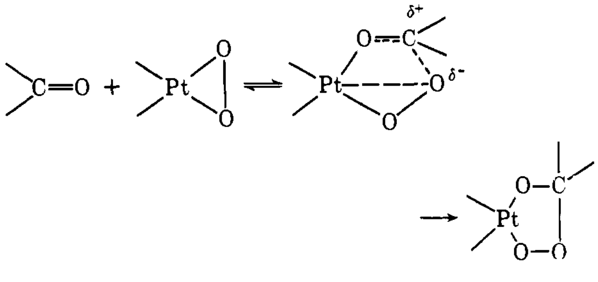


Figure 4. Plots of $1/k_A$ and $1/k_B$ vs. dimethylformamide concentration for the reaction with acetone in benzene at 30 ± 0.1 °C, [(PPh$_3$)$_2$PtO$_2$] = (1.4 ± 0.3)10^{-3} M.

tone > methyl isobutyl ketone > methyl ethyl ketone (Table V).

The reactivity of cyclic ketones also follows the same order (cyclobutanone > cyclohexanone > cyclopentanone > cycloheptanone, Table V) which has been observed for their reaction with sodium borohydride.[15] A similarity between the mechanisms of the borohydride reduction[16] and the insertion into the PtO$_2$ moiety would suggest that in the transition state for the reactions studied here there is not only coordination of the ketone to the platinum atom but also some bond formation between the PtO$_2$ moiety and the carbonyl group as shown in (B). This hypothesis is supported by the fact that activation



(B)

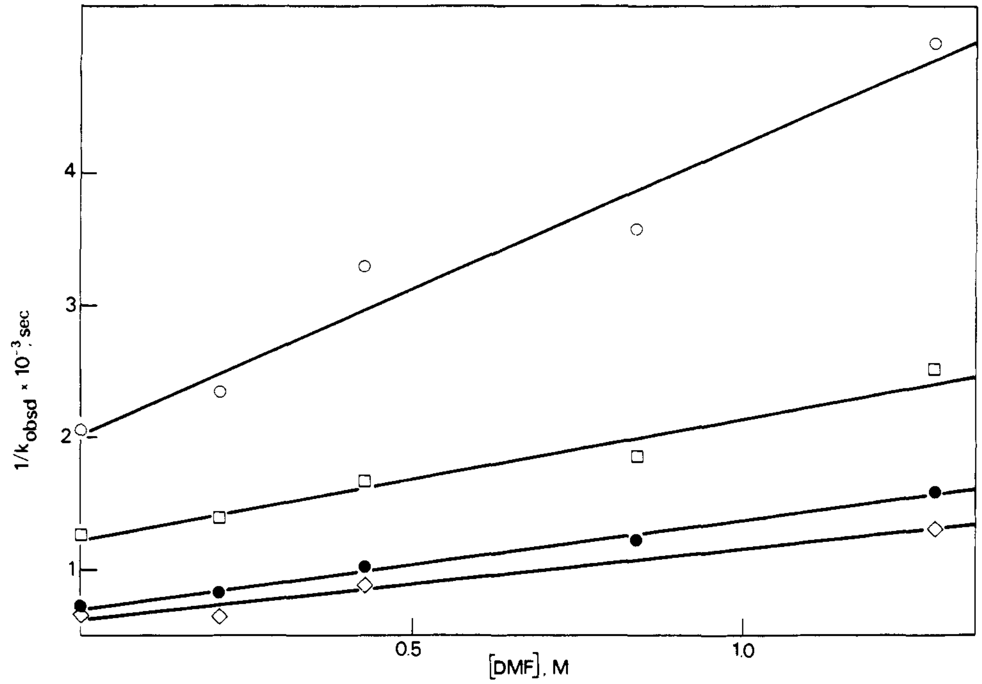


Figure 5. Plot of $1/k_{obsd}$ vs. dimethylformamide concentration at various acetone concentrations in benzene at 30 ± 0.1 °C, $[(PPh_3)_2PtO_2] = (1.4 \pm 0.3)10^{-3}$ M. [acetone] (M) ○, 0.26 ± 0.04; □, 0.48 ± 0.04; ●, 0.89 ± 0.06; ◇, 1.08 ± 0.03.

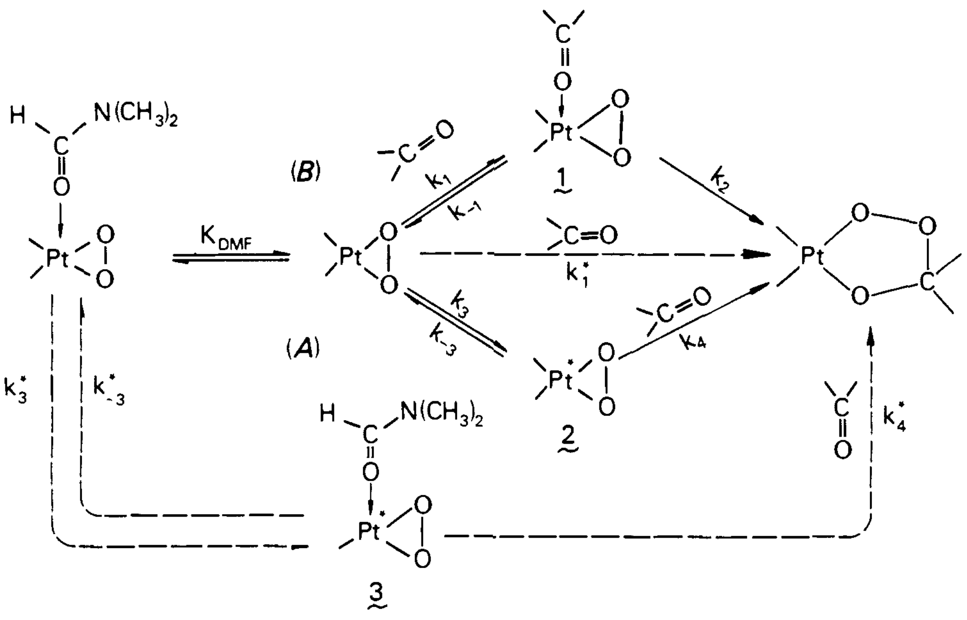


Figure 6. Reaction scheme; pathways described by dashed lines are not observed.

parameters for the two reactions are comparable. For both the borohydride reduction and the platinum-assisted ketone insertion into $Pt(PPh_3)_2O_2$ $\Delta H^{\ddagger}$ is between 8 and 13 kcal/mol and $\Delta S^{\ddagger}$ is between −30 and −43 eu (Table IV). The activation parameters for nucleophilic substitutions involving a platinum(II) complex are slightly different[17] ($\Delta H^{\ddagger}$ is between 10 and 20 kcal/mol; $\Delta S^{\ddagger}$ is between −15 and −30 eu). Also for the nucleophilic substitution reactions of platinum(II) complexes the formation of the new bond between the platinum atom and the entering nucleophile is the dominant aspect of the rate-determining step, with very little breaking of the bond between the platinum atom and the ligand which is to be expelled from the coordination sphere. As a consequence, the lower values of the enthalpy of activation found for the ketone insertion into $Pt(PPh_3)_2O_2$ are in agreement with a certain amount of concomitant bond breaking of the PtO_2 moiety in the activated complex.

Solvent basicity does not play the predominant role in the pathway involving intermediate **1** (path B in Figure 6), although the solvent can compete with the incoming ketone for the vacant coordination site at platinum; solvent polarity is more important in this pathway. For instance, two solvents of different basicity[18] but comparable polarity[19] such as dimethylformamide and propylene carbonate produce similar values of k_B (Table VI). When the polarity effect of the solvent is expressed by parameters such as K^{20} or E_T,[19] the values of log k_B are nearly linear with respect to these particular parameters. The best linear correlation was obtained with the parameter E_T. A trend corresponding to a decrease in the reaction rate with increasing solvent polarity was observed (Figure 7). This trend is not that which would be expected for a rate process in which a large charge separation is produced in the transition state but suggests some bond making between the peroxidic dioxygen and the coordinated ketone in such a

Table IV. Activation Parameters of Acetone Reaction in Different Solvents

reaction	solvent	dielectric constant,[a] 25 °C	DN,[b] kcal/mol	E_T,[c] kcal/mol 25 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
BH_4^- reduction[d]	2-propanol	18.3		48.6	8.8	−39.1
insertion	benzene	2.3	0.1	34.5	8.8	−42.4
(path B)	acetonitrile	37.5	14.1	46.0	11.9	−36.6
	THF	7.4	20.0	37.4	12.7	−30.7
dipolar addition	benzene	2.3	0.1	34.5	17.0	−20.3
(path A)	acetonitrile	37.5	14.1	46.0	29.0	15.4
	THF	7.4	20.0	37.4	13.8	−32.4

[a] Reference 18. [b] DN = donicity or donor number (ref 18). [c] E_T = molar transition energy (ref 19). [d] Reference 15.

Table V. Reactivity of Ketones in the Nucleophilic Attack on the Platinum Atom, Temperature 30 °C in Benzene as Solvent

ketone[d]	$k_B \times 10^4$, $M^{-1}\,s^{-1}$	$k \times 10^4$, $M^{-1}\,s^{-1}$ [a]
1,1,1-trifluoroacetone	>1000[b]	
acetone	14.0 ± 0.3[c]	15.1
methyl isobutyl ketone	7.88 ± 0.41[b]	
methyl ethyl ketone	6.37	
cyclobutanone	>1000[b]	266
cyclohexanone	183	161
cyclopentanone	39.5	7.01
cycloheptanone	17.7 ± 0.4[b]	1.02

[a] Values reported for the reduction with $NaBH_4$ in 2-propanol at 0 °C (ref 15). [b] Calculated from the equation $k_{obsd} = k_A + k_B[\text{Ket}]$ where $k_A = (1.27 \pm 0.18)10^{-4}\,s^{-1}$ (average value). [Ket]: see Table IIS. [c] Values in other solvents: 8.16 (THF); 6.68 ($CHCl_3$); 2.28 (1,2-dichloroethane); 1.71 (CH_3CN); 1.84 (propylene carbonate); 1.69 (DMF). [d] From the reported keto-enol equilibrium constants (see in the series S. Patai, Ed., "The Chemistry of Functional Groups", J. Zabicky Ed., "The Chemistry of the Carbonyl Group", Vol. 2, Interscience, New York, 1970, p 163) the resulting concentration of the enol in our experimental conditions can be considered generally too low to be important; in addition, the double bond in the enolic form would be not sufficiently activated to react with the platinum center (see ref 5).

Table VI. Influence of Solvent Basicity and Polarity on the Insertion of Acetone at 30 °C

solvent	DN,[a] kcal/mol	K,[b] 25 °C	E_T,[c] kcal/mol, 25 °C	$k_A \times 10^5$, s^{-1}	$k_B \times 10^4$, $M^{-1}\,s^{-1}$
DMF	26.6	0.480	43.8	1.36	1.69
propylene carbonate	15.1	0.489	46.6	0.266[d]	1.84

[a] DN = donicity or donor number (ref 18). [b] K = Kirkwood dielectric function $(\epsilon - 1)/(2\epsilon + 1)$ (ref 20). [c] E_T = molar transition energy (ref 19). [d] Values in other solvents: 3.79 (THF); 2.68 ($CHCl_3$); 1.65 (1,2-dichloroethane); 1.40 (CH_3CN).

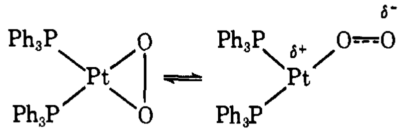
Table VII. Influence of Methanol on the Rate Constants with Acetone as Incoming Ketone at 30 °C[a]

[methanol] $\times 10^3$, M	$k_A \times 10^4$, s^{-1}	$k_B \times 10^4$, $M^{-1}\,s^{-1}$
none	1.27 ± 0.18	14.0 ± 0.3
8.5	2.55	28.0
48.0	14.4	71.4
195	49.4	133

[a] Solvent: benzene + methanol.

way that the formation of a pseudocyclic transition state can circumvent the otherwise large charge separation. In addition it is quite clear that any important charge separation which originates in the transition state can be dissipated by the large platinum complex, thereby producing some leveling of solvation effects.

The parallel pathway A shown in Figure 6 involves the slow formation of an activated form of the dioxygen complex (species **2**) which reacts rapidly with the ketone. The values of $\Delta H^{\ddagger}$ for this pathway, measured in different solvents (Table IV), are always higher than those for the pathway previously discussed, which involved the coordination of the organic carbonyl group to the metal. An initial isomerization of the coordinated dioxygen with formation of an end-on bonded dioxygen, as shown in eq 8, is a plausible first step in this pathway.



(8)

The relatively high values of $\Delta H^{\ddagger}$ found in all the solvents examined are not inconsistent with the necessary lengthening or even cleavage of a Pt-O bond. However, the large negative values obtained for $\Delta S^{\ddagger}$ (Table IV) cannot be explained by the simple breaking of a Pt-O bond but they rather imply a significant amount of reorganization within the solvation sphere.

On one hand, the overall rate of reaction decreases in the presence of a polar aprotic solvent and this effect is more pronounced in the pathway involving the dipolar intermediate **2** of reaction 8 (Figure 7), in which the platinum atom becomes more coordinatively unsaturated. Consequently, polar donor solvents can strongly solvate the transition state **2** not only by means of dipolar interactions but also by coordinatively saturating the metal center. In agreement with this assumption, k_A is dependent on both polarity and basicity (see Table VI). Using acetonitrile as solvent the value for k_A lies well off the appropriate straight line shown in Figure 7 and the related $\Delta S^{\ddagger}$ is significantly positive (Table IV). The reason for this discrepancy is not readily apparent at present.

On the other hand, the overall rate of reaction dramatically increases in the presence of methanol (Table VII). This appears to be a consequence of the possible presence of hydrogen bonding between the solvent and the coordinated peroxide ligand in the transition states **1** and **2**. Hydrogen bonding would be expected to weaken the platinum-dioxygen bond and consequently to stabilize transition states **1** and **2**[21] and this would result in an enhanced reaction rate. The fact that the ratio k_A/k_B for various methanol/benzene mixtures increases with increasing methanol concentration (Table VII) suggests that hydrogen bonding plays a more important role in stabilizing intermediate **2** than **1**. In fact the former is more polar and resembles a 1,3 dipolar species; it is then expected that the carbonyl group of a ketone can readily undergo addition to a 1,3 dipolar unsaturated structure.[22]

Conclusions

The results of the kinetic investigation discussed above show that dioxygen, when coordinated to platinum, can react by two

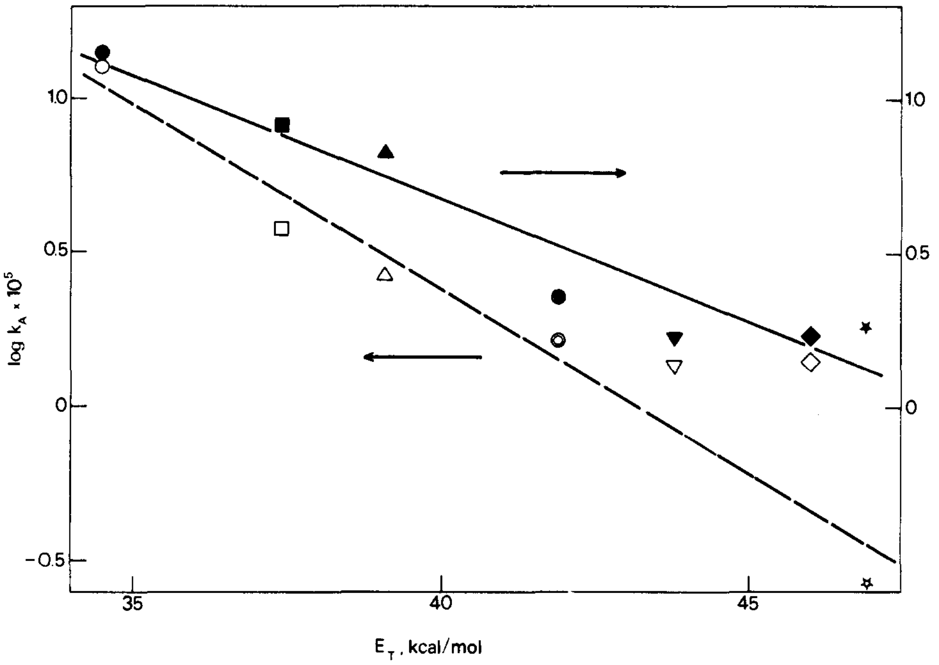


Figure 7. Dependence of the rate constants k_A and k_B on the polarity of the solvent with acetone as incoming ketone at 30 ± 0.1 °C. E_T = molar transition energy (ref 19); ○, benzene; □, THF; △, chloroform; ⊙, 1,2-dichloroethane; ▽, DMF; ◇, acetonitrile; ★, propylene carbonate.

different mechanisms with relatively weak electrophiles such as ketones to produce platinum(II) ozonide complexes. The major pathway does not involve an extra activation of dioxygen, but only the prior coordination of the donor electrophile to the platinum center.

The high reactivity observed for formally d^8 square planar platinum and palladium dioxygen complexes toward relatively weak electrophiles such as carbon dioxide,[23] nitric oxide,[24] activated olefins,[5] ketones, and aldehydes[3,4] must therefore be attributed to the coordinatively unsaturated nature of these d^8 complexes. On the other hand, the same complexes do not react with nonactivated olefins.[5] Accordingly the important feature involved in this pathway is the ability of the metal to enhance the electrophilic character of the incoming ligand through coordination. This is illustrated by the molybdenum(VI) complexes, $MoO(O_2)_2L_2$ (L is a polar donor solvent), which are formally d^0 complexes and which can stoichiometrically epoxidize cyclohexene.[25] The proposed mechanism for this particular reaction involves a prior coordination of the olefin in a cis position with respect to a coordinated dioxygen ligand. Our mechanistic investigation here suggests that the inability of simple olefins[5] such as cyclohexene to insert into $M(PPh_3)_2O_2$ (M = Pt, Pd) species is probably related to the absence of any kinetically relevant interaction of these particular olefins at the fifth coordination site of the complex, while the facile insertion of activated olefins (e.g., tetracyanoethylene) into $Pt(PPh_3)_2O_2$ can be attributed both to the tendency of this class of olefins to stabilize well-defined five-coordinated complexes of platinum[26] and to their greater electrophilic character. The minor pathway involves an "activation" of the dioxygen moiety bound to platinum. Although we have no definitive evidence regarding the true nature of the "activated form" of $Pt(PPh_3)_2O_2$, there is some evidence for an equilibrium between the side-on and end-on forms of the bonding of the dioxygen group supported also by other investigations.[24] This is probably an important mechanism for reactions of coordinatively saturated complexes,[27,28] although it has not been proved (but not completely discounted) for the insertion reaction of $(CF_3)_2CO$ on the completely saturated dioxygen complex $Ir(PPh_3)_2(CO)Cl(O_2)$, probably because this pathway is too slow to be detected for dioxygen complexes of iridium.[28] In this instance, the insertion reaction occurs only with strong unsaturated electrophiles such as sulfur dioxide[27] or perfluoro ketones[28] and does not require prior coordination to the metal center. In these latter cases the mechanism of the insertion could also involve direct external electrophilic attack of the ketone at the side-on coordinated dioxygen.[28,29] The reversible equilibrium proposed in reaction 8 is relevant because it could be involved at the surface of silver catalysts used for the heterogeneous ethylene epoxidation with dioxygen.

Work in this particular field supports the presence of surface dioxygen species as selective epoxidation reagents.[6] It is also quite probable that the cyclic structure of the metal ozonide is a surface intermediate in the epoxidation, as suggested by the characterization of such species in gold matrices treated with dioxygen and ethylene.[30] Spectroscopic data at different temperatures are also in agreement with the presence of both end-on and side-on dioxygen species on the silver surface.[31] Our work suggests that, owing to the high temperature of the surface reaction, the two types of dioxygen species can be in rapid equilibrium.

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Supplementary Material Available: Tables IS, IIS, and IIIS, a listing of k_{obsd} for different ketones in different solvents and at different temperatures (7 pages). Ordering information is given on any current masthead page.

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A Kinetics Study of the Oxidation of Iron(II) by Nitric Acid

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Abstract: The kinetics of the ferrous-nitrate clock reaction have been studied by spectrophotometric and potentiometric techniques at high acid concentration (0.6–2.0 M), ionic strength 2.1 M, and temperature 23 ± 1 °C. Our results as well as those of earlier thermodynamic and kinetics investigations on related systems are used to construct a reaction scheme, the rate equations of which are numerically integrated. The overall reaction $3Fe^{2+} + 4H^+ + NO_3^- \rightleftarrows 3Fe^{3+} + 2H_2O + NO$ can be followed by monitoring the absorbance of the $FeNO^{2+}$ intermediate which is formed, or the potential of the Fe(III)/Fe(II) couple. The observed time, t_{max}, to the absorbance peak at 450 nm varies inversely as $[H^+]_0^2[NO_3^-]_0/[Fe^{2+}]_0^{0.6}$. Added oxynitrogen intermediates accelerate the reaction, while dissolved oxygen is an inhibitor. The reaction scheme consists of seven principal reactions, three of which describe the reduction of nitrate to nitric oxide by ferrous ion, one for the formation of the $FeNO^{2+}$ complex, and three additional reactions which summarize the chemistry of oxynitrogen species in nitric acid solutions. The seven rate equations were integrated numerically, which permitted a computer simulation of the reaction profile. Each calculation required the specification of a set of rate constants and a set of initial concentrations for the seven independent species. All but two of the rate constants were available from the literature; in addition the calculation required the specification of the NO_2 solubility β and a parameter C_0 determining the initial HNO_2 (always present) concentration. The simulations revealed that the major factor which determines t_{max} is the rate of the reaction between nitric oxide and nitrate, which is the rate-determining step (with rate constant k_7) in a sequence of reactions which leads to the oxidation of Fe^{2+} and which is autocatalytic in NO. The model is moderately sensitive to the rate constant for the initial attack of nitric acid on ferrous and to the free parameters C_0 and β, but it is extremely sensitive to the value of k_7. Thus, the data should determine k_7 rather accurately (to a factor of 2), if the basic features of the model are correct. Autocatalytic shutdown occurs when $[HNO_2]$ becomes large enough so that nitrous acid is consumed more rapidly by second-order disproportionation than by reaction with ferrous. Thus, addition of oxynitrogen intermediates to the initial reaction mixture provides a quicker way to build up $[HNO_2]$ to a level where autocatalysis is shut down.

The reaction of ferrous ion with nitric acid has been employed as an analytical tool for well over a century.[1] The formation of a colored ferrous–nitric oxide complex provides the basis for the well-known brown-ring test[2] for the qualitative analysis of nitrates and nitrites. In the absence of a catalyst, the reaction begins quite slowly,[3] rendering it unsuitable for quantitative work, though addition of molybdate greatly accelerates the reaction, making possible accurate determination of nitrate.[4] If the uncatalyzed reaction is allowed to proceed, the rate of disappearance of Fe(II) increases and the color rapidly deepens until the solution suddenly returns to a colorless state. Thus the reaction is a clock reaction, which is apparently autocatalytic.[5]

Surprisingly, the kinetics of the ferrous–nitric acid reaction have not yet been subjected to systematic study. One investigation[5] exists in which the dependence of the reaction time on reactant concentrations was probed, but no explanation was suggested for the data obtained. The related reaction of Fe(II) with nitrous acid has been studied in some detail, primarily by Abel and co-workers,[6] and some data are also available on the kinetics of various reactions involving the oxynitrogen species which are present in nitric acid solution.[7-9] The kinetics of formation and dissociation of the $FeNO^{2+}$ complex have been determined.[10]

In this paper, we present a kinetics study of the Fe(II)-HNO_3 reaction. We have measured the rate of the reaction at various concentrations of the reactant species and of several likely intermediates. These results as well as those of earlier thermodynamic and kinetics investigations on related systems are used to construct a reaction scheme. The rate equations of this scheme are then integrated numerically. This procedure enables us both to compare our model with experiment and to

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