and as a further example structure VII, one of the 24 ortho polar structures, is represented by

$$\Phi_{\mathrm{op}}(1,\ldots,6) = \mathrm{p}_2(1)\mathrm{p}_2(2)\mathrm{p}_3(3)\mathrm{p}_4(4)\mathrm{p}_5(5)\mathrm{p}_6(6) \times (\alpha_1\beta_2 - \alpha_2\beta_1)(\alpha_3\beta_4 - \alpha_4\beta_3)(\alpha_5\beta_6 - \alpha_6\beta_5)$$

In each case p_i refers to the atomic p_π orbital centered at the *i*th carbon nucleus with no delocalization or orthogonalization. This gives, in effect, a mixed MO–VB calculation which we believe is the first of its kind.

The 175 individual valence bond functions are then grouped into 22 $^1A_{1g}$ symmetry functions, among which are two covalent (I, II), six singly polar (III–VIII), 11 doubly polar, and three triply polar $^1A_{1g}$ types. Consequently, our "full π" VB calculation corresponds exactly to the "full π" MO–CI fixed basis calculation done by Buenker, Whitten, and Petke,[9] and the ground state and 21 excited $^1A_{1g}$ energies for these two calculations are identical. The ground-state energy is given in Table I.

Table I. Comparisons of Various VB Calculations

	Functions	*E*, au	(*E* − SCF), au (kcal)
Covalent (I + II)	2	−230.3026	+0.0728 (+45.7)
SCF		−230.3754	0.0 (0.0)
Ortho ionized (VII, VIII)	2	−230.3781	−0.0027 (−1.7)
Covalent and singly ionized (I–VIII)	8	−230.4373	−0.0619 (−38.8)
"Full"	22	−230.4546	−0.0792 (−49.7)

In addition to the "full π" calculation, a series of smaller calculations was done to determine the importance of specific valence bond functions. The diagonal energy obtained for each covalent and singly polar *symmetry function* is listed in Chart I. For convenience, as was noted above, we have included a representative Rumer diagram for each function type.[10]

It should be noticed that the Kekule (I) and Dewar (II) forms have a higher energy than the ortho singly polar function (VII). The importance of these polar functions is shown further in a series of smaller calculations given in Table I. If one includes the covalent functions only, the energy obtained is 45.7 kcal above the SCF. If one includes the ortho polar functions only the energy is slightly lower than the SCF. However, including functions I–VIII the calculated energy was 38.8 kcal below the SCF and 84.5 kcal below the energy obtained with just the covalent functions. The occupation numbers obtained in this last calculation are listed in Chart I. The occupation numbers show very clearly the importance of the polar valence bond functions; the Kekule function (I) is listed fourth in importance and considerably below the two ortho polar functions.

The stability and importance of the singly polar functions in this calculation appears surprising and shows a definite disagreement with the calculation done by Craig.[2] However, Weinbaum[11] showed, in the VB treatment of the hydrogen molecule, that there is approximately 20% contribution to the wave function and a 5.5 kcal lowering in the energy, when the polar function is included. An analogy can be made with this calculation in explaining the importance of the polar functions to benzene. The correct $^1A_{1g}$ functions involve structures such as VII and VIII averaged around the ring. Such averaging corresponds to roughly 33% polar and 67% covalent character in the functions of this one type. Such averaging is, of course, impossible within one function type in H_2 where there are only two electrons but obviously improves the energy calculation for benzene. Other aromatic systems, including heteronuclear molecules, admit these kinds of mixed polar–covalent structures, and it seems likely that symmetric averages of these will be found to be more stable than purely covalent functions.

Among several points of interest brought out by this study is that the energy expectation values of the Kekule and Dewar structures are closer in the *ab initio* than in the semiempirical treatments, and this puts these structures on a much more competitive basis in this calculation than in previous ones. Many studies have been given (see, for example, Pullman[12] and Coulson[13]). However, these studies are restricted to the intercomparison of Kekule and (generalized) Dewar types. Since the present study indicates that the covalent types are of relative unimportance in benzene, it is possible the same situation may apply to the larger systems and, hence, it may be necessary to reopen these questions.

Furthermore, it has been argued on the basis of simple electrostatics that the farther separated charges are in VB structures the higher energy they have. Examination of IV shows that this trend is followed here, but a more careful analysis also shows that distance cannot alone account for the large differences found, and hence other phenomena must also be involved.

Finally, it is admitted that the Kekule structures alone seem to work very well in explaining chemical stability and reactivity in aromatic systems. The effect the present results will have on the existing concepts of resonance is not known. However, further work is being carried out on benzene and other aromatic systems, which will be published shortly. It is hoped this work will help to clarify the situation.

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(9) R. J. Buenker, J. L. Whitten, and J. D. Petke, *J. Chem. Phys.*, **49**, 2261 (1968).

(10) A listing of all covalent and ortho polar structures and the different symmetry functions is given in ref 2.

(11) S. Weinbaum, *J. Chem. Phys.*, **1**, 593 (1933).

(12) A. Pullman, *Ann. Chim. (Paris)*, **2**, 5 (1947).

(13) C. A. Coulson, *Proc. Roy. Soc., Ser. A*, **207**, 91 (1957).

(14) NDEA Predoctoral Fellow, 1972–1973.

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Kinetics and Mechanism of Oxidative Addition of Iodine to Platinum Acetylacetonate in Nonpolar Solvents. The Photochemically Initiated Free-Radical Chain Pathway

Sir:

Some important oxidative addition reactions of coordinatively unsaturated metal complexes with simple

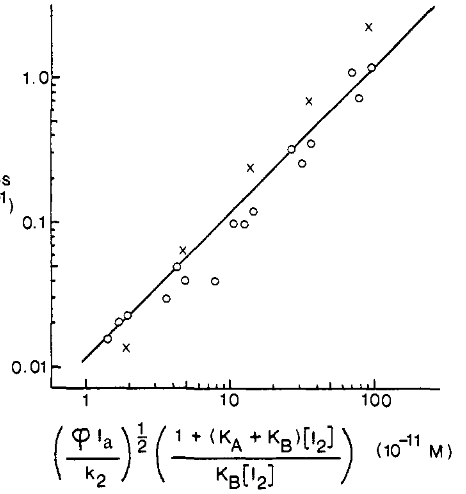

Figure 1. Rate data from photochemically initiated runs in CCl_4 at 20.5°: ○, 296 nm; ×, 446 nm.

covalent molecules occur *via* free-radical mechanisms.[1] We report kinetic data on the first example of this type of reaction in which the addition is chain propagated. This mechanism occurs in the reaction between $Pt(acac)_2$ and iodine in nonpolar solvents.

$$Pt(acac)_2 + I_3 \rightleftharpoons \textit{trans}\text{-}Pt^{IV}(acac)_2I_2$$

The stereochemistry and stoichiometry of the solid state and solution reaction was determined by a single-crystal X-ray diffraction study in conjunction with various spectroscopic techniques.[2] We now report that the reaction in solution proceeds *via* a 1:1 Lewis acid–base adduct intermediate, $Pt^{II}(acac)_2(I_2)$ (A), which is rapidly formed prior to the oxidative addition reaction which yields *trans*-$Pt^{IV}(acac)_2I_2$ (B). An unusual feature of the reaction is that the formation of B was photochemically catalyzed by the light beam used to monitor the reaction spectrophotometrically.

The photochemically catalyzed reaction was monitored with a stopped-flow spectrophotometer[3] at either of the band maxima[2] (296 and 446 nm) of B. The reaction in CCl_4 solution has the following characteristics at temperatures near ambient.

(i) Very rapid reversible reaction occurs within the mixing time of the reactants (~2 msec) to yield an intermediate which absorbs at 296 nm but not at 446 nm. The absorbance–concentration data at 296 nm show that only a species of stoichiometry $Pt(acac)_2(I_2)$ (A) is formed in significant concentration ($K_A = [A]_e/[Pt(acac)_2]_e[I_2]_e$: $\Delta H°_A = -65.3$ kJ mol^{-1} and $\Delta S°_A = -123$ J K^{-1} mol^{-1}). This initial reaction is followed by the slower reversible reaction which yields B ($K_B = [B]_e/[Pt(acac)_2]_e[I_2]_e$: $\Delta H_B = -65.3$ kJ mol^{-1} and $\Delta S_B = -126$ J K^{-1} mol^{-1}). It is not fortuitous that ΔH_A and ΔH_B are identical (*vide infra*).

(ii) In the presence of an excess of iodine ($[I_2]_T \geq 10[Pt]_T$), the rate of formation of B is first order[4] in the concentration of either $Pt(acac)_2$ or A: $d[B]/dt = k_{obsd}[Pt(acac)_2] = k_{obsd}[A]$.

(iii) At constant initial reactant concentrations k_{obsd} is proportional to the square root of the incident beam flux (I_0) both at 296 and at 446 nm: $k_{obsd} = kI_0^{1/2}$. No thermal pathway significantly contributes to k_{obsd}.

(iv) At 9.8°, where the initial reaction of $Pt(acac)_2$ to give A is almost stoichiometric, k_{obsd} is proportional to the square root of the amount of light absorbed per unit time by iodine molecules.

$$k_{obsd} = k'I_a^{1/2}\{I_a = I_0(1 - 10^{-\epsilon_{I_2}l[I_2]})\}$$

These data are consistent with the following chain mechanism

$$I_2 + h\nu \longrightarrow 2I\cdot$$

$$I\cdot + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + I\cdot$$

$$2I\cdot \xrightarrow{k_2} I_2$$

Any pathways involving the feasible five-coordinate Pt(III) chain carrier $Pt(acac)_2I\cdot$ are of negligible importance.[5] However, the data do not of course rule out propagation steps which involve the Pt(III) intermediate $(I_2)Pt(acac)_2I\cdot$. At the stationary state of iodine atoms the above mechanism gives[6]

$$k_{obsd} = k_1\left(\frac{\varphi I_a}{k_2}\right)^{1/2}\left\{\frac{1 + (K_A + K_B)[I_2]}{K_B[I_2]}\right\}$$

A plot of this relationship is depicted in Figure 1 for the data at 20.5° (21 runs). The chain length of these runs at the attainment of the stationary state lies in a range of 3000–150,000. Similar data were obtained at 9.8 (16 runs) and 31.3° (14 runs). Values of k_1 calculated from the above relationship are $(1.52 \pm 0.14) \times 10^9$, $(1.14 \pm 0.07) \times 10^9$, and $(1.86 \pm 0.18) \times 10^9$ l. mol^{-1} sec^{-1} at 9.8, 20.5, and 31.3° respectively. These rate constants and the low activation energy of about 10 kJ mol^{-1} show that the reactions of iodine atoms with A and with B ($k_1/k_{-1} = K_B/K_A = 0.694$) are diffusion controlled.[10]

These kinetic data are in excellent agreement with

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[1] J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966); J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970); J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972), and references cited therein.

[2] P. M. Cook, L. F. Dahl, D. Hopgood, and R. A. Jenkins, *J. Chem. Soc., Dalton Trans.*, 294 (1973).

[3] The absolute beam flux incident on the reaction solution in a Durrum Model 110 spectrophotometer was calibrated with a Hewlett-Packard Model 8334 radiant flux detector. The Durrum slit-control was used to vary the incident beam flux over a range of 6×10^{-18} to 7×10^{-12} einstein sec^{-1} at 296 nm and a range of 3×10^{-15} to 7×10^{-12} einstein sec^{-1} at 446 nm. These beam fluxes were measured with the spectrophotometer photomultiplier.

[4] The reactions exhibited an induction period due to the time of attainment of the stationary state (*vide infra*).

[5] The following elementary reactions involving the Pt(III) chain carrier, $Pt(acac)_2I\cdot$ (C·), were considered: $Pt(acac)_2 + I\cdot \rightleftharpoons C\cdot$; $C\cdot + I_2 \rightleftharpoons B + I\cdot$; $C\cdot + I\cdot \rightarrow B$; and $2C\cdot \rightarrow Pt(acac)_2 + B$. Rate laws for various combinations of these steps were derived by using the stationary-state approximation for the concentrations of C· and I·. A statistical analysis of the kinetic data showed that none of these processes significantly contribute to the observed rates.

[6] φ is the primary quantum yield of iodine atoms.[7,8] The values measured by Lampe and Noyes[7] at 436 nm were used to analyze the data at 446 nm. At 296 nm we estimated φ from data reported by Noyes, *et al.*[7,8] These estimated values are 0.44, 0.48, and 0.53 at 9.8, 20.5, and 31.3° respectively. Values of k_2 were calculated from the data of Aditya and Willard.[9]

[7] F. W. Lampe and R. M. Noyes, *J. Amer. Chem. Soc.*, **76**, 2140 (1954).

[8] L. F. Meadows and R. M. Noyes, *J. Amer. Chem. Soc.*, **82**, 1872 (1960).

[9] S. Aditya and J. E. Willard, *J. Amer. Chem. Soc.*, **79**, 2680 (1957).

[10] E. F. Caldin, "Fast Reactions in Solution," Blackwell, Oxford, 1964.

the thermodynamic data reported above. The ratio of K_A to K_B is indeed independent of temperature ($\Delta H°_A = \Delta H°_B$) as predicted by the relationship $K_B/K_A = k_1/k_{-1}$ and the diffusion controlled nature of both k_1 and k_{-1}.

The rate of attainment of the stationary state is also consistent with the mechanism. Excellent linear plots of the relationship

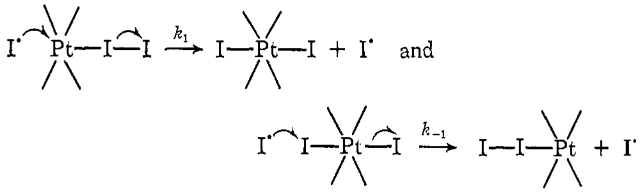
$$\ln\left(\frac{A_0 - A_e}{A_t - A_e}\right) = k_{\mathrm{obsd}}\int_0^t\left(\frac{e^{mt} - 1}{e^{mt} + 1}\right)\mathrm{d}t$$

(where A is absorbance and $m = 4(\varphi I_a k_2)^{1/2}$) were obtained. These data also predict that the reaction should exhibit a pronounced photo after effect. This was investigated by monitoring a reaction solution with a very low-beam flux subsequent to its irradiation with a light pulse of much greater flux. Very large photo aftereffects were observed. In some cases the reaction went to equilibrium before the iodine atom concentration had decayed to a steady concentration. These data give $k_1 = 1.7 \times 10^9$ l. mol^{-1} sec^{-1} at $-0.9°$ in good agreement with the stationary-state values.

The effect of radical initiators and inhibitors was investigated. Addition of O_2, DPPH, hydroquinone, and allyl iodide had negligible effects on the rates. This insensitivity to chemical additives probably results from the rapidity of the rates of reaction of iodine atoms with A and B.

The kinetics of the reaction in cyclohexane are very similar to those of the reaction in CCl_4 and give $k_1 \simeq 1 \times 10^9$ l. mol^{-1} sec^{-1} at 20.6°. On the other hand the cyclohexane system exhibits a thermal pathway (k''), $k_{\mathrm{obsd}} = k'' + k'I_a^{1/2}$, and its mechanism is currently being investigated.

Previous studies[11] of the structures of 1:1 halogen complexes with n donor atom (N, O, S, and Se) Lewis bases indicate that the most probable structure of A would contain a linear Pt–I–I arrangement which coincides with the principal axis of the planar $Pt^{II}(acac)_2$ moiety. An empty σ^* orbital on the iodine molecule is of correct symmetry to accept electron density from the d_{z^2} orbital of the platinum atom.[12] The very rapid reversible propagation step is consistent with this structure in that facile iodine atom attack can occur along the principal axis of either A or B.



It is of interest that the adduct $Pt^{II}(CN)_4(Br_2)^{2-}$ has been postulated[13] as a transient intermediate in the oxidative addition reaction: $Pt(CN)_4^{2-} + Br_2 \rightleftarrows$ *trans*-$Pt(CN)_4Br_2^{2-}$. Adducts formed between Lewis acids and coordinatively unsaturated basic metal complexes may be of considerable mechanistic importance in oxidative addition reactions.

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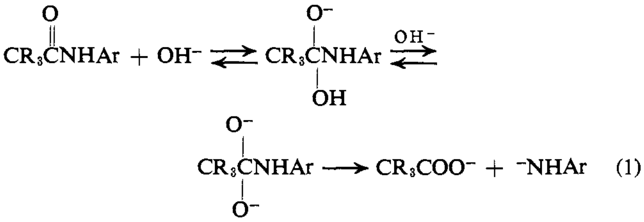
[14] Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY, United Kingdom.

Specific Base–General Acid Catalysis of the Alkaline Hydrolysis of *p*-Nitrotrifluoroacetanilide

Sir:

The mechanism of the alkaline hydrolysis of anilides with strongly electron-withdrawing ring substituents has been a subject of considerable interest lately.[1–4] It was originally proposed that these anilides hydrolyze by a pathway involving expulsion of a negatively charged anilide ion from a dianion intermediate without the aid of a general acid catalyst (eq 1).[1] This



$$\mathrm{CR_3\overset{\overset{\displaystyle O}{\|}}{C}NHAr + OH^- \rightleftarrows CR_3\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}NHAr \overset{OH^-}{\rightleftarrows} CR_3\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}}NHAr \longrightarrow CR_3COO^- + {}^-NHAr} \qquad (1)$$

interpretation was based on work with *p*-nitroacetanilide and *p*-formylacetanilide, which are not hydrolyzed at convenient rates in moderately basic solution, so that the possibility of general catalysis was not examined directly. Recently, Menger and Donohue[4] have found that the alkaline hydrolysis of *N*-acetylpyrrole shows similar kinetic behavior to *p*-nitroacetanilide and *p*-formylacetanilide. Since *N*-acetylpyrrole reacts considerably faster than acetanilides they were able to search for general catalysis. The finding of no observable general catalysis of this reaction confirms the previously proposed mechanism for ring-activated anilides.[1]

We have now examined the alkaline hydrolysis of the highly reactive *p*-nitrotrifluoroacetanilide and find that, contrary to expectations, this reaction *does* show kinetic general base catalysis. We interpret this result to mean that there are two pathways for cleavage of the tetrahedral intermediate. In addition to cleavage of the dianion to give *p*-nitroanilide ion and trifluoroacetate ion without general catalysis, a second mode of breakdown exists which involves cleavage of the monoanion *with* general acid catalysis to give *p*-nitroaniline and trifluoroacetic acid directly. These two pathways involve loss of the negative *p*-nitroanilide ion from the dianion intermediate but loss of neutral *p*-nitroaniline

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