

Figure 2. Dependence of k_{obsd} on the ligand concentration. Part A: dependence studied at pH 4.5, 30° , $\mu = 1.00$, $[\text{Ru}(\text{NH}_3)_5\text{OH}_2]^{2+} = 0.5 \times 10^{-4} M$. Part B: pH 1.0, 30° , $\mu = 1.00$ (lithium *p*-toluenesulfonate), $[\text{Ru}(\text{NH}_3)_5\text{OH}_2]^{2+} = 1.0 \times 10^{-4} M$.

virtually disappears, the observed rate constant reduces simply to k_1 . Experimentally, $k_1 = 2.4 \times 10^{-3} \text{ sec}^{-1}$.

At high $[\text{H}^+]$ the term $KK'[\text{MPz}^+][\text{H}^+]$ prevails in the denominator and expression 2 becomes

$$k_{\text{obsd}} = k_2 + k_1/K'[\text{H}^+] \quad (3)$$

Comparing with expression 1 and using the previously obtained k_1 value we calculate $k_2 = 2.1 \times 10^{-4} \text{ sec}^{-1}$ and $K' = 8.9 \times 10^2 M^{-1}$. By substituting these values in expression 2, an association constant $K = 16 M^{-1}$ was found. The curves in Figure 2 can be generated substituting in expression 2 the values given for k_1 , k_2 , K , and K' .

According to the mechanism given above the quotient of the product concentration, $[\text{P}]$, over $[\text{R}]$, the concentration of ruthenium(II) lost by a redox process, would be given by

$$[\text{P}]/[\text{R}] = k_1/k_2K'[\text{H}^+] \quad (4)$$

On studying the variation of $[\text{P}]/[\text{R}]$ with $[\text{H}^+]$ and assuming $[\text{R}] = [\text{Ru}(\text{II})_{\text{total}}] - [\text{P}]$ we found excellent linear dependence on the inverse of $[\text{H}^+]$, expressed by eq 5.

$$[\text{P}]/[\text{R}] = 1.3 \times 10^{-2}/[\text{H}^+] \quad (5)$$

Comparing expressions 5 and 4, and using for k_1 and k_2 our previous values, we calculated $K' = 8.7 \times 10^2 M^{-1}$ in agreement with the result found using eq 3.

Independent evidence for the existence of the intermediate was found in a competitive kinetic study at pH 4 based on the expectation that intermediate formation would reduce the free concentration of aquopenta-

ammineruthenium(II) by a factor $1/(1 + K[\text{MPz}^+])$. At pH 4.0, $T = 30^\circ$, k_{obsd} for the reaction of $6.0 \times 10^{-5} M$ aquopentaammineruthenium(II) with aqueous pyrazine (0.100 M) was $9.0 \times 10^{-3} \text{ sec}^{-1}$. In the presence of the added component 0.25 M *N*-methylpyrazinium ion, k_{obsd} was $4.9 \times 10^{-3} \text{ sec}^{-1}$ (measured at 493 nm, the isosbestic point for the two products). Although the presence of *N*-methylpyrazinium provides an additional path for consumption of reactant Ru(II), the rate of reaction is actually diminished by the presence of that ligand. From these measured rate constants the value of the formation constant for the intermediate is $10 M^{-1}$ while that found in the previous considerations was $16 M^{-1}$. The difference is outside experimental error and suggests that the intermediate has some reactivity with respect to pyrazine.⁶

A temperature dependence study in the 11–37° range at pH 4.5 before and after kinetic saturation in the ligand concentration gave the activation parameters for the step k_1 , $\Delta H^\ddagger = 18.4 \pm 0.5 \text{ kcal/mol}$ and $\Delta S^\ddagger = -10 \pm 2 \text{ eu}$, and for the equilibrium process K , the values $\Delta H = -5.7 \pm 1 \text{ kcal/mol}$ and $\Delta S = -17 \pm 3 \text{ eu}$.

The entropy change associated with formation of the intermediate is, as expected, unfavorable because of decreasing entropy of solvation. We suggest that the enthalpy of complexation, -5.7 kcal/mol , is largely due to the interaction of filled ruthenium(II) t_{2g} orbitals with low-lying acceptor orbitals of the ligand. This interpretation is consistent with the fact that in the product complex the $t_{2g}-\pi^*$ interaction is unusually strong.^{1,7}

(6) The observed distribution of products gave a clear indication that the reactivity of the intermediate is affected by the added heterocycle, and this effect, as well as other properties of the intermediate, is under investigation in this laboratory. Nevertheless, the competitive experiment shows unequivocally that the presence of *N*-methylpyrazinium ion markedly retards the rate of Ru(II) complexation.

(7) The experimental results do not distinguish between an intermediate of the "inner" or of the "outer-sphere" type. The authors, seeing a similarity between the activation enthalpy measured for the k_1 step and values of ΔH^\ddagger which have been measured for processes in which water in the ion $[\text{Ru}(\text{NH}_3)_5\text{OH}_2]^{2+}$ is replaced by various N heterocycles,⁵ favor the interpretation that the interaction is of the "outer-sphere" type.

(8) The authors gratefully acknowledge financial support from the following: the Conselho Nacional de Pesquisas, the Fundação de Amparo a Pesquisa do Estado de São Paulo (H.E.T., Predoctoral Fellowship), the Atlantic Petroleum Company of Brazil, the Agency of International Development, the National Science Foundation, the National Academy of Sciences and the Atlantic Richfield Corporation of the U. S. Also acknowledged gratefully are the aid and encouragement of Professors Ernesto Giesbrecht and Henry Taube.

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Received January 25, 1972

Triplet Energies, Reduction Potentials, and Ionization Potentials in Carbonyl-Donor Partial Charge-Transfer Interactions. I

Sir:

Charge-transfer (CT) type complexes¹⁻¹² have been proposed as intermediates in the photoreduction and

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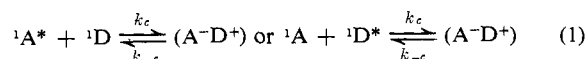
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quenching of triplet ketones and aldehydes. They have been written in A^-D^+ formulations, sometimes with wide separation of charge, but they have not been observed directly. Weller, *et al.*,¹³⁻¹⁷ have reported a quantitative relationship between kinetics of quenching by electron transfer and thermodynamic properties of aromatic hydrocarbon-amine pairs. We wish to report that certain properties of triplet carbonyl-donor complexes may be similarly related to the triplet energy,³ $\Delta E_{0,0}$, and the reduction potential, $-E(A^-/A)$, of the carbonyl compound, A, and the ionization potential, IP , of the electron donor, D, and that most of these complexes show only partial charge transfer.

In nonpolar solvents the free-energy change, ΔG_e , for charge-transfer (ion pair) formation in a singlet excited state, *i.e.*, anthracene-diethylaniline, eq 1, may be



represented by eq 2, obtained from published relations,¹⁵

$$\Delta G_e = -{}^1\Delta E_{0,0} + [E(D/D^+) - E(A^-/A)] - T\Delta S_e + 3 \text{ kcal/mol} \quad (2)$$

in which $E(D/D^+)$ is the oxidation potential of the donor. Entropy changes, ΔS_e , were fairly constant, ~ -18 cal/(deg mol), and may be included in a constant term. In acetonitrile direct formation of the solvated ions was the process of lower energy.¹⁴ When the free energy for this process, ΔG_{ET} , is greater than 5 kcal/mol it is equal to the free energy of activation for electron transfer,¹⁴ ΔG_{ET}^\ddagger , and there is a linear free-energy relation between ΔG_{ET} and the rate constant for ion formation. Such relations may be applicable¹⁴ to the corresponding triplet state reactions, and to charge transfer in nonpolar media. Use of more readily available ionization potentials of the donors in place of oxidation potentials only changes the constant in eq 2, since¹⁷ for molecules of similar dimensions $IP = E(D/D^+) + \Delta G_{solv} + C'$, where $\Delta G_{solv} + C' = \sim 6.5$ eV against sce.^{18,19} This leads to eq 3. In

$$\Delta G_e \approx -{}^3\Delta E_{0,0} + IP_D - E(A^-/A) + C \quad (3)$$

the present application to quenching of triplet carbonyl compounds by electron donors, the acceptor is the component of lower triplet energy, and in most of the cases $\Delta G_e > 5$ kcal/mol for complete charge transfer. For a series of donors with a constant

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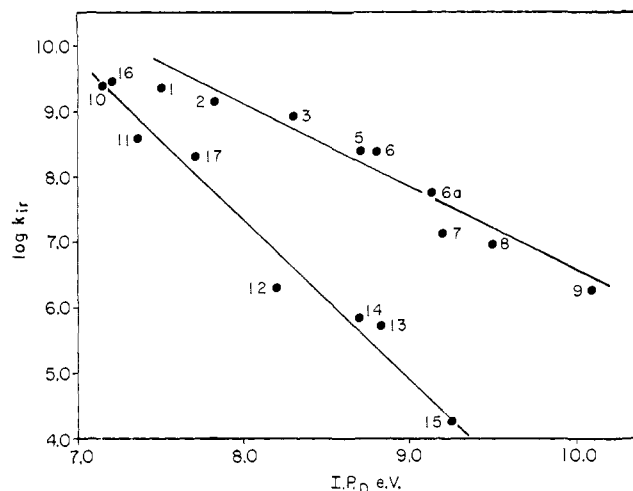


Figure 1. Relation of rate constant for quenching of benzophenone triplet, k_{ir} , to ionization potential of donor, IP_D . Numbers refer to the compounds of Table I.

acceptor, $\Delta G_e \approx IP_D + \text{constant}$, and for a series of acceptors with a constant donor, $\Delta G_e \approx -{}^3\Delta E_{0,0} - E(A^-/A) + \text{constant}$.

Rate constants, k_{ir} , for interaction of donors with triplet benzophenone were determined by quenching by naphthalene of photoreduction by the donor, or by quenching by the donor of the phosphorescence of benzophenone.^{1,2,4} Some results are summarized in Table I and Figure 1.

Figure 1 shows linear inverse relation between $\log k_{ir}$ and IP_D and supports a CT interaction mechanism. The data lie largely on two lines, one for aliphatic

Table I. Quenching of Triplet Benzophenone in Benzene

No.	Quencher	k_{ir} , $M^{-1} \text{ sec}^{-1}$ ^a	IP_D , eV ^b
1	Triethylamine	2.3×10^9 ^c	7.50
2	<i>N</i> -Methyl-2-butylamine	1.4×10^9 ^c	8.02
3	Di- <i>n</i> -butyl sulfide	8.3×10^8	8.30
4	Di- <i>tert</i> -butyl sulfide	5.0×10^7	
5	2-Butylamine	2.5×10^8 ^d	8.70
6	3-Methyl-2-pentene	2.4×10^8 ^e	8.80
6a	<i>cis</i> -2-Butene	8×10^7	8.13
7	<i>n</i> -Propyl mercaptan	1.3×10^7	9.20
8	Di- <i>n</i> -propyl ether	9.2×10^6 ^f	9.5
9	2-Propanol	1.8×10^6 ^e	10.1
10	<i>N,N</i> -Dimethylaniline	2.7×10^9 ^c	7.14
11	Triphenylphosphine	4×10^8 ^g	7.36
12	Anisole	2.1×10^6 ^f	8.2
13	Toluene	5.2×10^5 ^h	8.82
14	Diphenyl ether	7×10^5 ^f	8.70
15	Benzene	1.8×10^4 ⁱ	9.25
16	1,4-Diazabicyclo[2.2.2]-octane (Dabco)	2.9×10^9 ^j	7.2
17	1-Azabicyclo[2.2.2]-octane (Abco)	2.1×10^8 ^j	7.7

^a Based on diffusion-controlled rate constants of $6.3 \times 10^9 M^{-1} \text{ sec}^{-1}$ in benzene (W. D. Clark, A. D. Litt, and C. Steel, *Chem. Commun.*, 1087 (1969); *J. Amer. Chem. Soc.*, **91**, 5413 (1969)) and $1.1 \times 10^{10} M^{-1} \text{ sec}^{-1}$ in acetonitrile. ^b From ref 19. The value listed for 2 is that of diethylamine, for 3, that of di-*n*-propyl sulfide, and for 6, that of 2-methyl-2-butene. Values for Dabco and Abco were taken from A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49**, 1348 (1968). ^c From ref 4. ^d From ref 6. ^e From N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3265 (1968). ^f Unpublished results of C. Steel, A. Renner, J. B. Guttenplan, and S. G. Cohen. ^g From ref 9. ^h From A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963); neat toluene. ⁱ From Clark, *et al.*, footnote a. ^j Unpublished results of A. Parola and J. B. Guttenplan.

donors, another predominantly for aromatic donors, with least-squares slopes -0.067 ± 0.005 mol/kcal and -0.105 ± 0.006 mol/kcal, respectively. The rate constants for the most reactive compounds, **1**, **16**, and **10**, level off and may be approaching diffusion control. The values of slope are much lower than 0.74¹⁴ observed in systems in which quenching of fluorescence occurs *via* complete electron transfer, while the rate constants span the same range, 10^6 – 10^{10} $M^{-1} \text{ sec}^{-1}$. Only small solvent effects are observed. Values of k_{ir} for benzophenone–2-butylamine rise by a factor of 1.3 and for di-*n*-butyl sulfide by 2.0 in acetonitrile as compared with benzene, whereas the corresponding factor for fluorescence quenching involving full charge transfer is 13.¹³ The reduction potential of benzophenone is 1.73 V,²⁰ and from eq 2 and 3 it may be calculated that activation energies for transfer of a full unit of charge from most of the donors would be too great to lead to the high observed values of k_{ir} . This, the slopes, and the solvent effects indicate that these interactions of excited benzophenone with electron donors involve only partial transfer of charge, and may be rapid because of mixing with partial transfer of α H. The low reactivity of the bicyclic amine Abco and of di-*tert*-butyl sulfide is consistent with such a mixed process. Their values of k_{ir} increase by factors of 5.7 and 2.7, respectively, as solvent is changed from benzene to acetonitrile, indicating somewhat larger, but still partial charge transfer. Partial charge transfer enhances intersystem crossing from excited triplet to ground-state singlet, as it may enhance crossing from excited singlet to excited triplet.²¹ That 2-propanol (**9**) lies on the line may further indicate that interaction with both α H and *n* electrons is a general mechanism for interaction with such aliphatic compounds. Polar contribution to stabilization of the transition for abstraction of hydrogen from alcohols,¹ and abstraction of H from amines *via* CT interaction, may differ as the process starts and be similar at the transition state.

The aromatic compounds show lower ionization potentials and generally lower values of k_{ir} than their aliphatic analogs. These values show more sensitivity to *IP*, indicating a higher degree of charge transfer. Interaction with aromatic donors may be predominantly with the π electrons²² of the highest occupied molecular orbital, with less interaction with α H, if that is present, in the transition state.

A related study of interaction of a π, π^* excited triplet with a series of donors, and the application of the second relationship, $\log k_{ir} \approx (-^3\Delta E_{o,o} - E(A^-/A)) + C''$, to interaction of acceptors of varied excited state configurations with a constant donor will be published elsewhere.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission, AT(30-1) 2499.

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Received October 12, 1971

Reactions of Iron Atoms with Unsaturated Hydrocarbons

Sir:

We wish to outline the reactions of iron atoms with unsaturated hydrocarbons, to describe some new experiments which further illustrate the chemistry of metal atoms, and to report the synthesis of several novel organometallic compounds by the metal atom codeposition technique.

Iron atoms were obtained by resistively heating alumina or zirconium oxide crucibles containing iron powder (>99% Fe) to 1500° at a pressure of 10^{-3} Torr or less. The atoms then produced were cocondensed with hydrocarbons at -196° using the type of apparatus previously described for use in carbon atom reactions.¹

When iron atoms and 1,3-butadiene are cocondensed at -196° and the reaction mixture is warmed to room temperature, no volatile organometallic compound is obtained. However, a dark residue remains from which, under various conditions, it is possible to synthesize organometallic compounds by displacement.² Thus, if the reaction mixture is warmed to -78° , stirred 1 hr (at which temperature the residue is in suspension in the butadiene), and cooled to -196° , PF_3 or CO is added, and the mixture is warmed to room temperature, compounds of structure $\text{Fe}(1,3\text{-C}_4\text{H}_6)_2\text{L}$ can be isolated.

Bis(1,3-butadiene)trifluorophosphineiron(0) was obtained in 3.2% yield, as orange-yellow crystals: mp 185 – 192° dec (sealed tube); nmr (C_6D_6) multiplet τ 5.6 (4 H), multiplet 9.1 (4 H), multiplet 10.6 (4 H); mass spectrum (70 eV, 100°) $-m/e$ 252 (10%, M^+), 164 (55%), 110 (100%).

Bis(1,3-butadiene)carbonyliron(0) was isolated in similar yield: orange-red crystals; mp 130 – 137° dec (lit. 130 – 135°); mass spectrum and ir spectrum as reported.³

If the displacing π -acceptor ligand is removed at -78° , then volatile compounds containing more than one iron atom are also obtained. We believe that these may contain bridging butadiene ligands, which are displaced at higher temperatures, and that the dark involatile residue obtained if no π -acceptor ligand is added consists to a certain extent of chains of iron atoms bridged with butadiene ligands. In this way the iron atoms produced by vaporization are prevented from recombining and the residues obtained remain active toward reagents which do not react with bulk metal at these temperatures.

When iron is cocondensed with 1,3-cyclohexadiene and the mixture is warmed to -20° and stirred for 1 hr, catalytic disproportionation of the hydrocarbon to cyclohexene and benzene occurs. In a typical run, 4.4 mmol of iron was vaporized and converted 120 mmol of the cyclohexadiene into a mixture containing 33.4% cyclohexene, 30.2% cyclohexadiene, and 36.4% benzene. The known complex benzene(1,3-cyclohexadiene)iron(0) is also produced: red crystals; 1.7%

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