and another set longer than the equivalent type in Ni(TMP). This asymmetry, particularly the unexpected alteration of the C_a–C_m bond lengths, is indicative of a reduction in aromaticity of Ni(TMC) relative to Ni(TMP). This is dramatically illustrated in Figure 2, a view of each molecule down the N2–Ni–N3 plane. The extreme nonplanarity of the Ni(TMC) molecule is apparent. Deviations of the meso-carbon atoms from the least-squares plane through Ni, N1–N4, C1–C6, and C9–C20 are approximately 0.6 Å, far greater than in even the most puckered porphyrin skeletons. The present results are consistent with an asymmetric charge distribution, possibly resulting from charge transfer toward the reduced side of the chlorin. The nonplanarity here is to be contrasted with the essential planarity of the chlorin core in [2,3-dihydro-(α,β,γ,δ-tetraphenylporphyrinato)pyridine]zinc(II),[19] the only other metallochlorin structure known, and the near planarity of the chlorin core in phyllochlorin ester.[20] It is thus clear that chlorin systems show far greater structural variations than do the porphyrin systems, a possibly important biological factor.

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Reality of Electron Transfer in Slow Organic Reactions

Sir:

The idea that single-electron transfer may be involved in the rate-determining step of a variety of bimolecular organic reactions is a popular one and guides many current experimental investigations. In cases where the transfer would be expected to be exergonic, and the reactions occur at or near diffusion-controlled rates, there is no difficulty with the concept, and it is supported by numerous experiments, mostly involving photoexcited states. However, when slow reactions of large activation energy are involved, in which the transfer would be expected to be endergonic, there is considerable confusion as to how transition states should be formulated and what experimental criteria can serve to detect electron transfer in the rate-determining step.

A common observation in such systems is that, when the potential electron donor is varied with a common acceptor (or vice versa), plots of $RT \ln k$ vs. the one-electron oxidation potential of the donor (or acceptor) are linear (as might be anticipated) but with slopes considerably less than unity.

In one of the most explicit recent discussions of the problem, Schuster[1] has argued that such small slopes are entirely consistent with a rate-determining, irreversible endergonic electron transfer in the reactions involved. The purpose of this communication is to show that the argument leads to difficulties but that an alternative interpretation, possible electron transfer *after* the rate-determining step, can account for the quite compelling evidence[2] that at some stage in the reaction electron transfer has in fact taken place.

In Schuster's formulation, an endergonic irreversible electron transfer is written as

$$D + A \underset{}{\overset{K_{12}}{\rightleftharpoons}} D...A \xrightarrow{k_{23}} D^{+}\cdot...A^{-}\cdot \xrightarrow{k_{30}} \text{products} \qquad (1)$$

and he proposes that

$$k_p = K_{12}k_i e^{-\alpha\Delta G_{23}/RT} \qquad (2)$$

where k_p is the observed rate constant, k_i the rate constant for the electron transfer if it were isoergonic, ΔG_{23} the free energy change for the electron transfer, and α a proportionality constant which is also the slope of a $RT \ln k_p$ vs. oxidation potential plot.

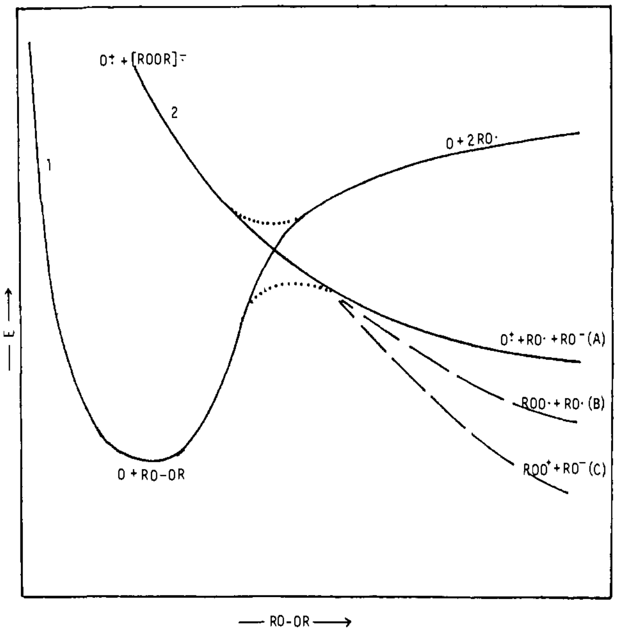

Figure 1. Plot of energy (E) vs. RO–OR bond length for reaction of a diacyl peroxide (RO–OR) with an electron donor (D).

Rewriting eq 2 in energy terms and simple algebra (eq 3) shows

$$\Delta G_p^{\ddagger} = \Delta G_{12} + \Delta G_i^{\ddagger} + \alpha\Delta G_{23} \qquad (3)$$

that, if $\Delta G_p^{\ddagger} > (\Delta G_{12} + \Delta G_i^{\ddagger})/(1 - \alpha)$, $\Delta G_p^{\ddagger} < \Delta G_{23}$, an obvious impossibility, which has also been noted, less explicitly, by Scandola and Balzani.[3] Since, as such reactions are usually considered, $\Delta G_i^{\ddagger}$ and ΔG_{12} should both be very small (ΔG_{12} might even be negative if any attractive forces exist between D and A), eq 2 and 3 should only be valid for very slightly endergonic processes. Indeed, this is in the region where the Marcus formulation already predicts $\alpha = 0.5$.

How then should we look at the rate-determining step in such processes when they are strongly endergonic and slow? Two approaches lead to a rather similar picture. First, we might assume that ΔG_{12} is really quite large, i.e., that D and A must be squeezed very tightly together, or that, if k_{30} refers to some sort of bond scission in A, the bond is highly stretched. Alternatively, we might consider that charge transfer is only partial in the transition state, so a modest attractive force or mutual polarization, similar to that in charge-transfer complexes, is generated, lowering the energy barrier. This, of course, is a very old idea—it is essentially the picture proposed by Greene when he first described the reaction of phthaloyl peroxide with donor olefins,[4] and is similar to the structures proposed in the 1940's to account for polar effects in general in radical reactions.[5-7]

To develop these ideas further, I will consider a typical example, the accelerated decomposition of diacyl peroxides in the presence of electron donors.[2,4,8] Figure 1 is a plot of energy vs. peroxide bond length, RO–OR, for such systems. As such, it is a cross section through a multidimensional surface of which another important coordinate is certainly RO–OR–D separation. It is accordingly assumed that, for each value of RO–OR, the RO–OR–D separation is that resulting in the lowest energy for the

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(8) Pryor, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 1582–1588.

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total system. Schuster's model apparently considers that this separation is large, and the reaction essentially follows curve 1 to the intersection and then curve 2. If changes in the oxidation potential of D result simply in vertical displacements of curve 2, this will indeed lead to $\alpha < 1$, with, to the extent that the curves may be considered linear in the region of intersection, a constant value.

The alternative approach assumes less separation and emphasizes the splitting of energy levels which occurs on crossover between two states of similar energy. Here the reaction should really follow the lower dotted curve between 1 and 2. Charge transfer is neither rate determining nor complete in the transition state, but its extent increases along the reaction coordinate to the products, A.[9]

This formulation suggests a very similar transition state for reactions leading to other quite different (transient) products, B and C. The reaction to C is simply a nucleophilic displacement by D on the peroxide bond, with an early, polarized transition state, while B represents a possible low-energy path for radical production.[10] The energy levels indicated for A, B, and C are arbitrary and will depend on the structures of RO–OR and D. In fact, more than one may be formed, or they may equilibrate, even within the original solvent cage.

How then can we hope to describe more exactly the reaction paths followed in these reactions? Product studies, including fast spectroscopic determination of transient intermediates, should distinguish reactions leading to A, B, or C. Here, Schuster has convincing evidence for (eventual) electron transfer to yield $D^{+\cdot}$ in some cases, and free radicals are sometimes detected.[11] However, in most systems, the observed products are most easily accounted for as the consequences of simple initial nucleophilic displacement.[12] Probing transition-state structures is more difficult, since "complete" and "partial" charge-transfer formulations lead to qualitatively similar predictions. Investigation of steric effects on rates should give some indication of the "tightness" or extent of bond formation in the transition state, and here an early study of benzoyl peroxide–phenol reactions has shown that ortho substitution markedly slows rates.[13] Similarly, several isotope labeling studies have shown that the carbonyl oxygen of acyl peroxides largely or completely retains its identity in reactions with amines,[14] phenols,[14] and electron-rich double bonds,[15] a result at least consistent with incipient bond formation in the transition state.

If reactions leading to A-, B-, and C-type products in fact occur through transition states of significantly different structure, one would expect them to show significantly different changes in rate with structure and other reaction conditions. As far as I know, this has not been demonstrated.[16]

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[9] Although electron transfer from donor to peroxide is strongly endothermic as indicated, electron transfer from electron-rich aromatics to an acyloxy radical is exothermic, so curves 1 and 2 cross. Thus, electron-rich aromatics may be electrolytically oxidized in the presence of carboxyylate anions; cf.: Sasaki, K.; Newby, W. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *20*, 137–165. Stated another way, increased electron density weakens RO–OR bonds. The rate of decomposition of benzoyl peroxides shows a negative Hammett ρ value: Swain, C. G.; Stockmeyer, W. H.; Clarke, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 5426–5434.

[10] A fourth process to simply yield $D + 2RO\cdot$ can be ruled out, since the back-reaction $2RO\cdot \rightarrow ROOR$ may be presumed to have negligible activation energy. Accordingly, the barrier to peroxide decomposition can only be lowered by coupling with some other process such as electron transfer or covalent bond formation.

[11] For example, the reaction of *m*-chlorobenzoyl peroxide and *p,p'*-dimethoxystilbene gives 10% scavengeable radicals: Greene, F. D.; Adam, W.; Cantrill, J. E. *J. Am. Chem. Soc.* **1961**, *83*, 3461–3468.

[12] Thus, aromatics commonly undergo acyloxy substitution, although the possibility that this arises from fast recombination of fragments from path A cannot be excluded.

[13] Walling, C.; Hodgdon, R. B., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 228–233.

[14] Denney, D. B.; Denney, D. Z. *J. Am. Chem. Soc.* **1960**, *82*, 1389–1393.

[15] Greene, F. D. *J. Am. Chem. Soc.* **1959**, *81*, 1503–1506.

[16] Although I have emphasized reactions of peroxides, a similar attempt to evaluate the significance of electron transfer in reactions between organometallic compounds and halogens etc. has been made by Kochi, e.g.: Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141–2152.

Hydrogenation of Carbon Monoxide to Methanol and Ethylene Glycol by Homogeneous Ruthenium Catalysts

Sir:

Conversion of synthesis gas—a feedstock derivable from many sources—to organic chemicals has become a very important goal within the chemical industry as world petroleum prices continue to rise. Homogeneous catalysis will serve a significant function in this framework if highly selective processes operative at low pressures can be developed. Although there are recent reports of homogeneously catalyzed CO hydrogenation at low pressures, rather low rates of product formation were observed.[1-3] Other published work in this area has been limited to high pressures, generally above 1000 atmospheres (atm). The first demonstration that organic products (including ethylene glycol and glycerine) could be obtained from H_2/CO by homogeneous catalysis was performed with cobalt catalysts under extreme pressures (1500–5000 atm).[4] Subsequently, rhodium catalysts were found to be catalytically active at elevated pressures, especially for conversion of synthesis gas to ethylene glycol,[5] and continued research on this system has given improved results at lower pressures.[6] Recently, a number of homogeneous catalysts (based on iron, ruthenium, and iridium) have been reported to hydrogenate carbon monoxide to ethylene glycol and/or methanol at pressures substantially above 1000 atm.[7-9] In contrast to these reports of catalysis under extreme conditions, we present here some initial studies of ruthenium catalysts at pressures of 340 atm and below, including the observation of homogeneous CO hydrogenation under moderate conditions, and a remarkable promoter effect of carboxylic acids on the formation of ethylene glycol by these catalysts. Since the completion of our original manuscript, essentially identical observations have appeared in a patent application.[10]

Reaction of acetic acid solutions of $Ru_3(CO)_{12}$ with mixtures of CO and H_2 at pressures above ca. 100 atm produces substantial quantities of methyl acetate and smaller amounts of ethylene glycol diacetate, as shown in Table I. Traces of glyercine triacetate have also been detected in these mixtures.[11] Significant obser-

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[1] (a) Thomas, M. G.; Beier, B. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 1296. (b) Demitras, G. C.; Muetterties, E. L. *Ibid.* **1977**, *99*, 2796.

[2] Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3623.

[3] Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45.

[4] (a) Gresham, W. F.; Schweitzer, C. E. (to DuPont) U.S. Patent 2 534 018, 1950. (b) Gresham, W. F. (to DuPont) U.S. Patent 2 636 046, 1953.

[5] Pruett, R. L.; Walker, W. E. (to Union Carbide Corp.) U.S. Patent 3 833 634, 1974.

[6] For example, see: Kaplan, L. (to Union Carbide Corp.) U.S. Patent 4 162 261, 1979, in which experiments at pressures below 550 atm are described.

[7] (a) Fonseca, R.; Jenner, G.; Kiennemann, A.; Deluzarche, A. In "High Pressure Science and Technology"; Timmerhaus, K. D., Barber, M. S., Eds.; Plenum Press: New York, 1979; pp 733–738. (b) Deluzarche, A.; Fonseca, R.; Jenner, G.; Kiennemann, A. *Erdoel Kohle, Erdgas, Petrochem.* **1979**, *32*, 313. (c) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359.

[8] Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

[9] Williamson, R. C.; Kobylinski, T. P. (to Gulf Research and Development Co.) U.S. Patents 4 170 605, 1979, and 4 170 606, 1979.

[10] Knifton, J. F. (to Texaco Development Corp.) UK Pat. Appl. 2024811, 1980.

[11] In addition to these products, ethyl acetate is also formed in reactions done in acetic acid. The ethanol is apparently derived largely from acetic acid by catalytic hydrogenation, since reactions in propionic acid solvent yield similar quantities of propyl propionate and only traces of ethyl propionate.

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