this case, it is believed that the hydrogen atoms are located over the edges, where, according to the symmetry classifications, orbitals principally from the metal of A_1, E, and T_2 species would be available for bonding to the six-hydrogen atom array whose orbitals are grouped in those same symmetry species.

The chemical reactions of I illustrate its unsaturated nature. Contact with any substance with well-developed donor power, including solvents such as ether and acetonitrile as well as the usual ligands such as CO or phosphines in hydrocarbon solution, brings about reaction at room temperature, in some cases, instantly. Most of these lead to degradation of the tetrahedral cluster. The reaction with CO yields $H_3Re_3(CO)_{12}$ and $HRe(CO)_5$ as the principal products. Use of isotopically labeled CO gives labeled products which, in the case of $H_3Re_3(CO)_{12}$, could assist in assigning the carbonyl modes and which, in turn, could indicate whether the substitution was stereospecific or not.

Treatment of I in cyclohexane solution in a heterogeneous reaction with $NaBH_4$ results in a very slow reaction in which the red color and all traces of I are observed to disappear from the hydrocarbon solvent. Removal of the cyclohexane and addition of acetone reveals (by ir) the spectrum of the $H_6Re_4(CO)_{12}{}^{2-}$ ion (2000 and 1910 cm^{-1}), a saturated compound previously isolated from the reduction of $Re_2(CO)_{10}$ with $NaBH_4$.

(7) (a) Address correspondence to this author; (b) publication no. 2651.

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Received June 29, 1970

Chemiluminescent Reactions of Iron and Nickel Carbonyls with Ozone

Sir:

While checking for possible interferences in the chemiluminescent detection of NO, spurious light emission was observed in the region of 5000–6500 Å when carbon monoxide was mixed with ozonized oxygen in a flow reactor. The light emission could be greatly reduced by passing the carbon monoxide over asbestos at 200° or through a Dry Ice trap. In the latter case, intense orange light was observed as the trap was warmed. Thus, the emission is not directly from carbon monoxide but is due to an impurity. A spectrum of this emission showed broad maxima at 5650, 5900, and 6200 Å, with some vibrational structure. From published spectra,[1] the luminescence observed here was identified as FeO emission with a small contribution from NiO. In addition, deposits of iron and nickel oxides were found on the reactor walls. These results clearly indicate that carbonyl impurities, commonly present when carbon monoxide is stored in steel tanks, are responsible for the light emission. This was further confirmed with $Fe(CO)_5$ and $Ni(CO)_4$ samples. Emission of FeO and NiO has been observed previously in high-temperature flames[1] and in O-atom reaction of the carbonyls,[2] but no study of chemiluminescence in ozonolysis has been reported.

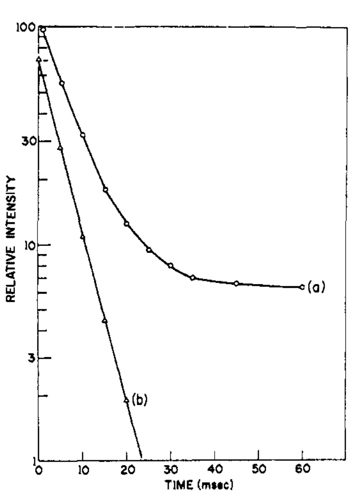

Figure 1. (a) Light emission from carbonyl containing carbon monoxide. (b) Light emission from $Fe(CO)_5$.

The kinetics and mechanism of the chemiluminescent reactions were studied by measuring the emission intensity as a function of reaction time and reactant concentration. Ozone was determined from the decay rate of the NO_2* emission from the well-known reaction $NO + O_3 \rightarrow NO_2^* + O_2$. When carbon monoxide containing both iron and nickel carbonyl was treated with a large excess of ozone, the intensity of the unresolved spectrum showed an initial first-order decay followed by a very flat tail (Figure 1a). However, from the distinct spectral distribution of the two reaction zones, iron oxide was found to be responsible for the exponential decay while nickel oxide gives rise to the tail. This kinetic behavior of FeO and NiO emission was confirmed with pure samples as described below.

The orange FeO emission from the reaction of pure iron carbonyl in excess ozone followed first-order decay (Figure 1b) with a lifetime given by the relation $\tau = (k[O_3])^{-1}$, where $k = 1 \times 10^{-13}$ cc/(molecule sec). The lifetime was also shown to be independent of carbonyl concentration under the conditions used here. These results indicate that the light emission is closely coupled to the primary reaction of ozone with iron carbonyl. The reaction must be at least 58 kcal exothermic to provide energy for light emission of FeO at 5000 Å.

The NiO emission was observed with pure nickel carbonyl and ozone only in the presence of carbon monoxide. Since the light extends the entire length (50 cm) of the flow reactor with very little decay, kinetic measurements could not be made. With only ozone and nickel carbonyl, a black deposit indicates that a nonluminous reaction occurs under these conditions. The NiO emission can then be generated by adding carbonyl-free CO well downstream. This shows that a nickel-containing species produced in the nonluminous reaction travels some distance before it reacts with carbon monoxide to yield NiO chemiluminescence. The most likely species is ground-state NiO, which can be easily reduced by carbon monoxide. The reaction of ozone with nickel atoms is exothermic by 76

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(1) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," Wiley, New York, N. Y., 1963.

(2) W. R. Brennen, Ph.D. Thesis, Harvard University, 1964.

kcal, which is sufficient to account for the observed emission. In addition, this mechanism

$$\mathrm{NiO + CO \longrightarrow Ni(g) + CO_2} \qquad (1)$$

$$\mathrm{Ni(g) + O_3 \longrightarrow NiO^* + O_2} \qquad (2)$$

explains the observed extremely slow decay of the light intensity by regeneration of NiO*. A further study of the iron carbonyl–ozone reaction revealed that a similar effect could also be obtained from FeO* at a much greater concentration of carbon monoxide.

The results reported here may explain the light emission and initial fast reaction observed by other investigators studying the carbon monoxide–ozone system.[3]

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(3) J. Pressman, L. M. Arin, and P. Warneck, Final Report, Contract No. CPA 22-69-36, U. S. Public Health Service, NAPCA-CRC.

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Received July 30, 1970

Triplet Ketone–Olefin Interactions: Energy Transfer, Charge Transfer, or Radical Addition?

Sir:

The interactions of ketone triplets with olefins are of widespread interest;[1–7] nonetheless, no comprehensive study of the effects of olefin structure on the rate constants for quenching of triplet ketones has yet been reported. We have performed such a study and report here those results most pertinent to the question of the mechanism for the quenching interaction.

There seems little doubt that triplet benzene (E_T = 84 kcal) is quenched by olefins *via* very efficient electronic energy transfer.[8] This behavior is reasonable, since the vertical triplet excitation energy of ethylene is now generally accepted to be 82 kcal.[9,10] Triplet acetone (E_T = 78–80 kcal), on the other hand, seems to interact with 2-pentene by two competitive mechanisms: electronic energy transfer and revertible chemical addition.[3] The olefin apparently undergoes sensitized cis–trans isomerization both from its triplet and by cleavage of a metastable adduct. Kinetic evidence suggests that triplet acetophenone[3] (E_T = 73.5 kcal) and triplet benzophenone[2] (E_T = 69 kcal) sensitize the isomerization of olefins predominately *via* formation and fragmentation of metastable adducts.

The intermediacy of 1,4 biradicals in these ketone–olefin interactions is strongly suggested by the kinetic evidence for an intermediate which can fragment to ground-state ketone and (isomerized) olefin and by the competitive, nonstereospecific formation of oxetanes. In fact, most authors have suggested that the phenyl ketone triplets add directly to olefins to yield biradicals. Our results add support to the developing consensus that the triplets of phenyl ketones (E_T < 75 kcal) interact with acyclic olefins primarily by formation of a metastable adduct. However, we feel that a charge-transfer complex (or exciplex) precedes the biradical since the effects of olefin and ketone structure on quenching rate constants are inconsistent with radical-like additions.

We have measured the efficiency with which various olefins[11] quench the type II photoelimination of butyrophenone in benzene.[12] Table I lists the Stern–Volmer slopes and k_q values calculated from them. Table II compares our results with those in the literature for the k_q values of dichloro-, dialkyl-, trialkyl-, and tetraalkylethylenes toward various triplets.

Table II reveals a sharp decrease in quenching rates for the alkenes in going from benzene to acetone, as would be expected when energy transfer becomes endothermic or nonvertical. However, the further decreases in triplet energy of the phenyl ketones are accompanied by *increased* values of k_q. This reversal effectively rules out energy transfer as the rate-determining quenching process.

The effects of varying olefin structure on k_q (contained in Table I) do not parallel those on known rates of electrophilic free-radical additions.[13] For example, 1,1-dialkylethylenes are no better quenchers than 1,2-dialkylethylenes, and di-*tert*-butylethylene is no worse a quencher than *trans*-4-octene.

It has been established that alkoxy radicals serve as excellent models for the hydrogen abstraction reactions of n,π* ketone triplets.[14,15] The k_q values in Tables I and II are several orders of magnitude larger than what would be expected for alkoxy radical-like additions.[16] The 10–20-fold larger k_q values of the phenyl ketones compared to acetone do not parallel the similarity in reactivity displayed by these ketones in hydrogen abstraction reactions.[17] However, the electron-withdrawing phenyl groups would be expected to increase the electrophilicity of the n,π* triplet states.

We suggest that the sum of all available evidence is most consistent with the primary interaction between ketone triplet and olefin being formation of a charge-transfer complex, whenever energy transfer is so endothermic as to be negligibly slow. This complex presumably collapses to a biradical, the structure of which is determined by the orientation of ketone and olefin in the complex. The lack of predictable stereoselectivity in oxetane formation[1] is further testimony to the presence

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(1) For a review of early work, see D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(2) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

(3) J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

(4) R. A. Caldwell and S. P. Jones, *ibid.*, **91**, 5184 (1969).

(5) A. M. Braun, W. B. Hammond, and H. C. Cassidy, *ibid.*, **91**, 6196 (1969).

(6) N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

(7) R. E. Rebbert and P. Ausloos, *ibid.*, **87**, 5569 (1965).

(8) (a) M. W. Schmidt and E. K. C. Lee, *ibid.*, **91**, 5919 (1968); (b) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968); (c) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

(9) (a) C. Reid, *J. Chem. Phys.*, **18**, 1299 (1950); (b) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(10) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(11) All olefins were purified by preparative vpc; other methods do not remove trace impurities which increase the apparent quenching efficiency of many olefins, especially the cycloalkenes.

(12) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(13) (a) P. I. Abell, *Trans. Faraday Soc.*, **60**, 2214 (1964); (b) A. P. Stefani, L. Herk, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 4732 (1961).

(14) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

(15) P. J. Wagner and A. E. Kemppamin, *ibid.*, **90**, 5896 (1968).

(16) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1965); C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967).

(17) For example, compare P. J. Wagner, *ibid.*, **88**, 5672 (1966), with N. C. Yang and R. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).