ties for the ions involved. More sophisticated calculations might shed light in this question.

An examination of the data in Table I reveals that the chemical shifts for the ring carbons often move in a direction opposite to that expected on substituent changes. For example, replacing a H in benzene by a methyl group causes a shift of -3.1 ppm in the para position while the para-carbon (*i.e.*, C_1) shifts by $+4.9$ when the same substitution is made in the benzoylium ion. This behavior was rationalized[3] as being due to the large contribution of a "ketene like" resonance form (1). Such forms are known to be important from X-ray data.[13,14] However, ketene-like structures cannot explain the negative slope of the δ ^{13}C is charge density plot for *all* the ring carbons.

$$O=C-\langle\text{ring}\rangle^+$$

1
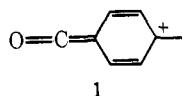
These results show that one cannot always expect to find a correlation between ^{13}C chemical shifts and σ. Also, while correlations of CNDO/2 charge densities with δ ^{13}C exist for neutral molecules and the theory seems to be well developed, the same is not true for charged systems. The occurrence of opposite correlation slopes within the same molecule points out dramatically the need for both more elegant calculations and more experimental work to elucidate fully the correlation between δ ^{13}C and charge densities in *charged systems*. Whether the fault lies with the calculations on charged molecules or at more basic levels, we are forced to the conclusion that correlations of ^{13}C chemical shifts with calculated charge densities in carbocations are not yet well understood and may fail. While we are not willing to generalize on the basis of this one system and universally condemn the use of ^{13}C NMR chemical shifts as an index of charge density, these results do make it clear that caution must be used in obtaining charge distributions from ^{13}C chemical shifts. More work should be done on simple cationic systems attempting to correlate ^{13}C NMR chemical shifts with various indicators of charge density in order to examine the general validity of the suggested relationship between charge density and chemical shift, and, if the relationship is valid, to calibrate it. These data also illustrate the danger of assuming correlations between electron distribution (or δ ^{13}C) and thermodynamic stability.[17]

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Thermodynamic Limitations in Chemiluminescent Reactions

Sir:

Despite the current interest in chemiluminescence, there is no clear understanding as to why some reactions are chemiluminescent and others are not. For example, thermolysis of 1,2-dioxetanes[1] leads to an excited-state ketone with a quantum yield approaching 1. In contrast, thermolysis of Dewar benzenes[2] leads to triplet-state benzene, but with a quantum yield of only 0.02–0.1%. These reactions seem quite similar, in that both lead from strained reactants to very stable products, with an exothermicity close to the energy of a visible photon. McCapra[3] and Kearns[4] have suggested that dioxetanes should be chemiluminescent because a ground-state orbital correlates with an excited orbital of the product ketones. Turro and Lechtken[5] have attributed the high chemiluminescent efficiency in thermolysis of dioxetanes to vibronic coupling during a concerted cleavage. Richardson et al.[6] have attributed the high yield to a rapid intersystem crossing of a biradical intermediate. Dewar[7] has suggested that high chemiluminescent efficiency requires a transition state with the highest occupied and lowest vacant molecular orbitals nearly degenerate. Yet there are also thermodynamic limitations on chemiluminescent yields, and a consideration of these limitations clarifies the contrast between dioxetanes and Dewar benzenes.

How can a reaction that is exothermic by only 60–71 kcal/mol[2,8] produce an excited state 78–85 kcal/mol[9] above the ground state? Obviously, the first law of thermodynamics must not be violated, and, in recognition of the first law, the accepted resolution of this apparent violation is that the energy difference comes from the activation energy, which is 22–28 kcal/mol[2,10] (Figure 1a). By such reasoning, reactions with an extremely high activation energy should be capable of converting thermal energy into light. For example, isomerization of norbornadiene should produce excited-state toluene, since the reaction[11a] is exother-
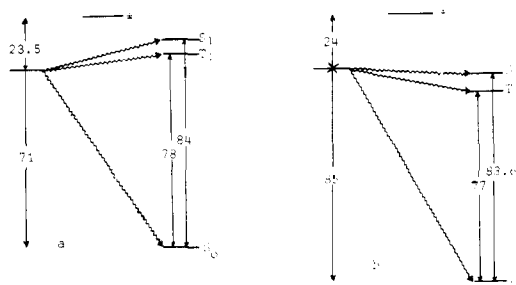

Figure 1. Energetics of reactant, transition state, and possible products in dioxetane thermolysis, which can produce excited singlet (S_1) and triplet (T_1) states: (a) enthalpy, in kcal/mol; (b) free energy, in kcal/mol, at 25°.

The Reaction of Methyl Radicals with Nitric Oxide

BY A. MASCHKE, B. S. SHAPIRO, AND F. W. LAMPE

RECEIVED OCTOBER 14, 1963

Methyl-d_3 radicals, formed by the photolysis of azomethane-d_6, react with nitric oxide by successive addition to form trimethylhydroxylamine-d_9. During this successive addition, nitrosomethane-d_3 is the sole product observed until nitric oxide consumption is essentially complete. Thereafter the successive addition of radicals to nitrosomethane-d_3 to form trimethylhydroxylamine-d_9 is in competition with ethane-d_6 formation by radical combination. A kinetic analysis of the data subsequent to nitric oxide consumption leads to a lower limit of 6.51×10^{-14} cm.^{3} molecule^{-1} sec.$^{-1}$ for the reaction $CD_3 + CD_3NO \rightarrow (CD_3)_2NO$.

In a recent communication[1] we reported some observations on the sequence of reactions occurring when methyl-d_3 radicals were formed by the room temperature photolysis of azomethane-d_6 in the presence of low concentrations (ca. 0.2–2%) of nitric oxide. It was shown that under these conditions nitrosomethane-d_3 is formed exclusively until depletion of nitric oxide is essentially complete. After the nitric oxide is consumed, trimethylhydroxylamine-d_9 and ethane-d_6 are formed in competing processes, the former presumably by successive addition of methyl-d_3 radicals to nitrosomethane-d_3 and the latter by methyl-d_3 radical combination. These findings were consistent with the work of Phillips[2] and Bromberger and Phillips[3] who found trimethylhydroxylamine as a product in their studies of the methyl radical abstraction of nitric oxide from methyl nitrite at 180°. The reaction sequence reported earlier[1] is also in agreement with Hoare's[4] recent studies of the acetone–nitric oxide photolysis at 200° in which it was found that between two and three methyl radicals were scavenged per nitric oxide molecule. Moreover, the reaction sequence found in the gas phase[1] appears to be analogous to the findings of Gingras and Waters,[5] that in solution three 2-cyano-2-propyl radicals add to each nitric oxide molecule.

This paper comprises a more complete report of our studies of the reaction sequence in the room temperature photolysis of azomethane-d_6–nitric oxide mixtures.

Experimental

Methyl-d_3 radicals were generated by the photolysis of azomethane-d_6 with light of wave length greater than 3100 Å. The photolyses were carried out at room temperature (ca. 25°) in a cylindrical cell, in one end of which was a gold-foil having a pin-hole leak into the ionization chamber of a Bendix Model 14-101 Time-of-Flight mass spectrometer. The opposite end consisted of a flat quartz window for admission of the light beam while the cylindrical wells were constructed of stainless steel. The apparatus is entirely similar to that described in detail by Heicklen and Johnston[6] except that we used a smaller pinhole (diameter of ~0.002 in.) and only a 3-l. reactant reservoir. We found that, with the time constant of 690 sec. of this pin hole leak, pressure diminution of reactants in the 3-l. reservoir was always less than 5% over the course of photolysis. Azomethane-d_6 was used to avoid the mass interference of nitric oxide and ethane at m/e 30.

In the first experiments the entire mass range up to m/e 100 was repeatedly scanned during photolysis. After the identity of product peaks had been established, the photolyses were conducted by continuously monitoring each product peak and the parent peak of azomethane-d_6 (m/e 64) simultaneously. The simultaneous measurement of the azomethane-d_6 parent peak and the various product peaks permitted the use of peak height ratios (product peak height to m/e 64) to determine product concentrations. Over the course of a photolysis the azomethane-d_6 concentration remains essentially constant[1] so that the ratio technique corrects for small fluctuations in electron beam current and electron multiplier sensitivity. In general, the mass spectrometer was operated with an ionizing electron energy of 50 e.v. and an electron trap current of 0.15 μa. A few experiments were conducted with a nominal electron energy of 18 e.v.

The light source was an Osram HBO-109 high-pressure mercury arc which has a low wave length cut-off at about 3100 Å. The spectral emission of the lamp and the wave length dependence of the azomethane absorption coefficient are such that the average effective wave length is about 3660 Å. The power supply to the lamp was of such a nature that reproducibility of the lamp current and, hence, of the incident intensity, was ~±20%.

Nitric oxide that had been obtained from the Matheson Co. was used as received. Azomethane-d_6, stated to have an isotopic purity of greater than 99%, was obtained from Merck Sharpe and Dohme, Ltd. Although this was received and stored in a darkened container, it was always found necessary to remove traces of the photolysis products ethane-d_6 and nitrogen before each set of photolyses. This was accomplished by several freeze–pump–thaw cycles using a freezing methanol slush as the cooling bath.

A direct calibration of m/e 36 from ethane-d_6 was not possible as the compound was not on hand. Instead we obtained the parent peak height–concentration relationship for ethane-d_6 using m/e 33 from 1,1,2-ethane-d_3. This introduces no significant error into our results because the ionic abundance of m/e 33 from 1,1,2-ethane-d_3 is within 2% of that of m/e 36 from ethane-d_6,[7] and no significant (i.e. >1%) differences in total ionization cross section are to be expected.

Results and Discussion

Photolysis of Pure Azomethane.—When pure azomethane-d_6 is photolyzed under our conditions, the only products observed are nitrogen and ethane-d_6. The formation of ethane-d_6 is indicated by the growth of m/e 36, the observation of which suffers no interference from the mass spectral peaks of azomethane-d_6. The formation of nitrogen is evident from the growth of the residual m/e 28 after corrections for the contributions from azomethane-d_6 and ethane-d_6 are made. Although we looked specifically for methane-d_4 and radical addition products of the $CD_3N{=}N$ radical, such products were present only at concentrations below the limit of our detection sensitivity. With ethane-d_6 and nitrogen being the only products observed, we can write for the photolysis mechanism of azomethane-d_6 under these conditions

$$CD_3N{=}NCD_3 + h\nu \longrightarrow 2CD_3 + N_2 \qquad (1)$$

$$CD_3 + CD_3 \longrightarrow C_2D_6 \qquad (2)$$
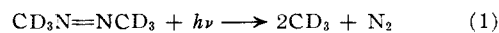
Methyl-d_3 radicals are at a concentration level much below our sensitivity of detection. Hence, in an kinetic treatment of our flow system we need not consider

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(25) A stronger limitation has also been derived,[15] on the assumptions that the reactions are uncoupled and reversible. However, the observed quantum yields[2] are in excess of this limitation.

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Addition of Methylene to Uncoordinated Double Bonds in Polyolefin Transition Metal π Complexes

Sir:

Research in the area of polycyclic metal π-olefin complexes has been stimulated by both interest in compounds of this type[1] and studies on how metals influence the thermal rearrangements of olefins.[2] This second aspect of the chemistry can also be a synthetic problem; that is, many reactions between polycyclic olefins and low valent transition metals produce products in low yields that frequently do not contain the 1:1 metal to olefin adduct.[3] This report describes preliminary results on a new synthetic approach to polycyclic metal complexes, the reaction of methylene with uncoordinated double bonds present in polyolefin metal π complexes. Other workers have demonstrated that the free double bonds in compounds like η^4-1,2,3,4-cycloheptatrieneiron tricarbonyl (1) are essentially unperturbed by the metal and will undergo electrophilic reactions[4] and catalytic hydrogenation.[5] On the other hand, olefinic character of coordinated double bonds is significantly reduced as shown from both X-ray studies[6] and the resistance of these bonds to catalytic hydrogenation.[7] Thus, it seemed reasonable that methylene would react exclusively with uncoordinated double bonds while the metal would prevent addition to coordinated double bonds. Successful reactions of this type could be developed into procedures in which the metal would direct the location of methylene addition.

One attempted methylene addition reaction on an organometallic molecule containing a free double bond has been reported by Johnson et al.[4] They treated 1 with the Simmons–Smith reagent,[8] but the product of the reaction was hexacarbonyl[bi(cyclohepta-2,4,6-trienyl)]diiron formed by hydrogen abstraction and not the CH_2 addition product. Precise experimental details were not given although the reaction was carried out in ether. Because the

addition of CH_2 to 1 would yield a known compound,[9] our investigation began with attempts to add CH_2 to this complex. Accordingly, 1 (11.6 mmol) was dissolved in ether (20 ml) and added dropwise to a refluxing ethereal solution (20 ml) of CH_2I_2 (58 mmol) over Zn/Cu couple (3.8 g) with a catalytic amount of iodine present. The resulting solution was refluxed for 2 days and then chromatographed on alumina to yield after solvent evaporation a yellow oil. This oil was shown to be bicyclo[5.1.0]octa-2,4-dieneiron tricarbonyl (2) (0.49 g, 23%) by comparing the ^1H and ^{13}C NMR and infrared spectra with those of an authenic sample.[9] None of the product obtained by Johnson et al.[4] was observed. From either preparation, of the two possible isomers of 2, the isomer that has been isolated has the cyclopropyl ring trans to the metal.[10] Thus, the methylene addition occurs anti to the metal in this case.
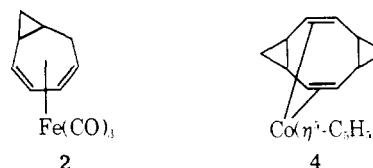
It was decided to demonstrate the generality of this synthetic approach by allowing two complexes to react that contain the same carbocyclic ring coordinated differently to two different metal systems. Thus, η^4-1,2,5,6-cyclooctatetraenecobalt (η^5-cyclopentadienyl) (3) (8.8 mmol) was dissolved in ether (20 ml) and added dropwise to a refluxing solution of CH_2I_2 (7.1 ml, 87.7 mmol) in ether (20 ml) over Zn/Cu couple (5.6 g) with a catalytic amount of I_2 present. After refluxing gently for 2 days, the ether was evaporated, the residue dissolved in hexane (20 ml), and this solution filtered and chromatographed on alumina (3 × 30 cm). Elution with hexane yielded after solvent evaporation a yellow solid that was shown from the high resolution mass spectrum to have the formula $C_{15}H_{17}Co$ (0.43 g, 19%) (calcd, 256.0660; found, 256.0632). The proton decoupled ^{13}C NMR spectrum has signals[11] at 83.9 assigned to the η^5-C_5H_5 carbons, at 65.6 assigned to four equivalent metal π-coordinated olefinic carbons, at 21.3 assigned to the four methine carbons of the cyclopropyl rings, and at 12.6 assigned to the methylene carbons.[12] This compound is thus formulated as η^4-2,3,7,8-tricyclo[7.1.0.0^{4,6}]deca-2,7-dienecobalt (η^5-cyclopentadienyl) (4), the addition product of 2 equiv of CH_2 to nonadjacent double bonds of the cyclooctatetraene ring in 3. Both of the cyclopropane rings are most likely cis to the metal although the above data do not rigorously establish this fact. No monoadduct was isolated or observed.

A reaction of η^4-1,2,3,4-cyclooctatetraeneiron tricarbonyl (5) (8.2 mmol) and the Simmons–Smith reagent (82 mmol) was carried out exactly as described above for the cobalt complex 3. Chromatography yielded a yellow fraction followed by a red fraction. The red fraction was starting material (ca. 0.4 g, 20%), while evaporation of solvent from the yellow fraction yielded a yellow solid that was shown from the high resolution mass spectrum to have the formula $C_{14}H_{14}FeO_3$ (0.59 g, 25%) (calcd, 286.0291; found, 286.0300), the product of addition of 3 equiv of methylene to 5. The following data show that this compound is best formulated as η^4-6,7,8,9-tricyclo[8.1.0.0^{3,5}]undeca-6,8-dieneiron tricarbonyl (6), pictured in Figure 1. The infrared spectrum in hexane solution showed carbonyl stretching bands (cm^{-1}) at 2035 1970, and 1960, similar but not identical with those of the starting material. The proton decoupled ^{13}C NMR spectrum is shown in Figure 1A. Figure 1B is the ^{13}C NMR spectrum of the d^6 analog