peroxylactone batch, the operator, and the fluorescer source. Occasionally a "wild run" was observed, but this was immediately obvious and discarded.

(11) Initial intensities (I_o) were obtained by extrapolation of the enhanced chemiluminescence intensity decay plots, standardized with the POPOP scintillation cocktail, and corrected for photomultiplier response and fluorescer reabsorption ad detailed in ref 2.

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Organic Photochemistry with High Energy (6.7 eV) Photons: Cis ⇌ Trans Isomerism in Cyclooctene

*Sir:*

In contrast to the numerous studies which have been conducted on the photochemical cis ⇌ trans isomerism in olefins at wavelengths longer than 200 nm,[1] there have been only a few reports of such investigations in the far-ultraviolet region. A recent study[2] of the direct photolysis of cyclooctene at 185 nm in solution drew attention to the high value (~1) of the ratio of the trans to cis isomer at the photostationary state. It was also observed that, in the initial stages of the reaction, there was negligible loss of the olefin by side reactions. No quantum yields were reported and the results were interpreted in terms of the $\pi \rightarrow \pi^*$ singlet state of the olefin.

We wish to report our results on a quantitative investigation of this system at the same wavelength which allows a more detailed examination of the excited state which may be involved in this process.

The strong absorption of *cis*-cyclooctene has a maximum at 185 nm and its extinction coefficient at 185 nm (1.0×10^4 L/(mol cm)) is almost exactly as large as that of *trans*-cyclooctene at this wavelength. The latter has a broad maximum in its ultraviolet absorption at ~196 nm.[3] At longer wavelengths, both molecules exhibit the weaker $\pi \rightarrow 3s$ Rydberg absorption.[4] Weak absorption extends down to 254 nm (cis, $\epsilon_{254} \sim 16$; trans, $\epsilon_{254} < 1$).

Irradiations were carrier out in pentane solution (2×10^{-2} M) using a 50-W mercury resonance lamp. To measure quantum yields, the light intensity at 185 nm was calibrated by using the gas phase conversion of oxygen to ozone ($\Phi = 2$) as the actinometer.[5] The rate of ozone formation was measured by standard iodimetry.[6] Quantum yields for both forward and reverse reactions in the photoequilibrium

$$cis\text{-cyclooctene} \underset{h\nu_{185}}{\overset{h\nu_{185}}{\rightleftharpoons}} trans\text{-cyclooctene} \qquad (1)$$
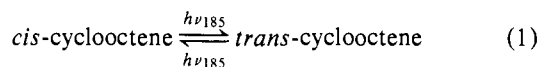
were extrapolated to zero conversion from the data in Figure 1. At $t = 0$, the quantum yields were equal to each other within experimental error (±5%) and equal to unity (±20%). Since there were small amounts of other products[2,7] which amounted to 5% of the *cis*-cyclooctene which disappeared, it is probable that the actual quantum yield for the forward reaction (1) is 0.95. We propose that this reaction can serve as a practical actinometer for solution phase photochemistry at 185 nm. The reaction is easy to follow by gas chromatography, the reactant (*cis*-cyclooctene) is readily available and inexpensive, and the solvent can be any saturated hydrocarbon of sufficient purity. Below concentrations of 4×10^{-2} M, no effect of concentration was evident.

The mercury resonance lamp that was used emitted radiation at 254 nm as well as at 185 nm. The light intensity at the former wavelength was ~6 times the value at the latter.[8] However, the effect of any parallel reaction due to absorption of 254-nm light during irradiation at 185 nm can be discounted
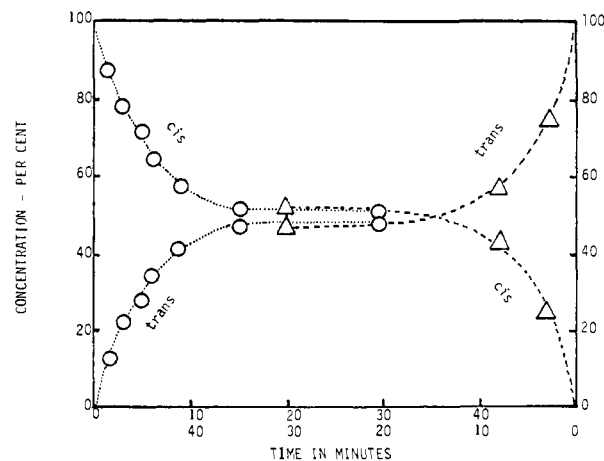

Figure 1. Composite diagram of percent interconversion of cyclooctene stereoisomers as function of time: 185-nm radiation; solvent pentane; concentration 10^{-2} to 10^{-3} M. Left ordinate and circles refer to reaction starting from 100% cis isomer. Right ordinate and triangles refer to reaction starting from 100% trans isomer.

since, at the concentrations and pathlengths that were used, the optical density for the *cis*-cyclooctene solution at 254 nm was ~0.05. Published work[2,9,10] indicates a highly unfavorable ratio of trans to cis isomer on irradiation (direct, sensitized, or catalyzed) at long wavelengths.

The significant point of interest in the present work is that $\Phi_{c \rightarrow t} + \Phi_{t \rightarrow c} \sim 2$ which indicates that a common excited state or intermediate is not reached during irradiation of either isomer at 185 mm. It further suggests that, for each isomer, from its excited state that is initially reached at this energy, a favorable path without barriers leads to the other isomer from which the latter can internally convert to the ground state, all steps being highly efficient. With this picture in mind, one can examine the energy diagram of olefins with a view to identify the source of these isomerizations.

Discussions of the photochemical reactions of olefins are invariably based on the mapping of the torsion coordinate as a function of energy for ethylene as given by Merer and Mulliken.[11] In the region from 200 to 175 nm, not only is there less than general agreement on anything but the most general features,[4] but shifts in the energy levels through alkyl substitution have also to be taken into account.

Both the $\pi \rightarrow \pi^*$ singlet and triplet states have similar energy profiles with a minimum at 90° of twist with the result that equilibration between the two isomers in their excited states seems unavoidable. Therefore, the present results cannot be accommodated by initial excitation to the $\pi \rightarrow \pi^*$ singlet as previously proposed.[2] The R states in the energy diagram of ethylene do have the profile stipulated before. The problem lies in locating these states in the spectrum of cis and trans cyclooctene.

A detailed analysis of the spectrum of *cis*-cyclooctene has not been carried out. Both the optical absorption and circular dichroism spectra of *trans*-cyclooctene have been analyzed in detail.[3] The band with a maximum at 196 nm has been assigned to the $\pi \rightarrow \pi^*$ singlet state. On the short wavelength side of it, at ~178 nm, a Rydberg absorption is clearly present as revealed in the circular dichroism spectrum. From a recent ab initio theoretical calculation on the circular dichroism spectrum of this compound, Liskow and Segal[12] have computed the energy levels of the Rydberg states in this region as $\pi \rightarrow 3P_y$, 6.62 eV, and $\pi \rightarrow 3P_x$, 6.39 eV, respectively. The geometry of the former state would be well suited to undergo the isomerization reaction studied here and its energy level would be accessible with the photon energy used.

Preliminary results[7] show that such an efficient cis → trans

photoisomerization takes place at 185 nm in other cyclooctene derivatives as well.

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Hydrocarbon Formation from Metal Carbonyl Clusters Supported on Highly Divided Oxides

Sir:

Recent publications have described the use of transition metal cluster carbonyl complexes in the catalytic reduction of carbon monoxide to alkanes[1,2] or alcohols[3] and in the water gas shift reaction[4] in the homogeneous phase, but the observed catalytic activities are very low under low pressures. We wish to report here our results relating to these two reactions in the heterogeneous phase, using transition metal carbonyl complexes supported on highly divided oxides. We have not only found an interesting reactivity but also quite different results when these were compared with supported metals or with metal clusters in the homogeneous phase, as far as the product distribution is concerned.

Impregnation of alumina, silica, or magnesia with various

Table I. Mass Balance between the CH_4 and CO_2 Formed and the Carbonyl Ligands When 10 mg of Cluster Supported on 200 mg of Al_2O_3 is Heated under Argon in a Sealed Glass Tube

Cluster	Temp, °C	Mol of CH_4/mol of cluster	Mol of CO_2/mol of cluster	(Mol of CH_4 + mol of CO_2)/mol of CO ligand
$Ru_3(CO)_{12}$	300	0.91	10.1	0.92
$Os_3(CO)_{12}$	400	0.30	11.8	1.00
$Os_6(CO)_{18}$	300	1.11	18.4	1.09
$Rh_4(CO)_{12}$	250	0.22	7.7	0.66
$Rh_6(CO)_{16}$	250	1.26	9.2	0.65
$Ir_4(CO)_{12}$	300	0.38	10.5	0.91

metal carbonyl clusters and subsequent heating of the supported *complex under argon or CO* results in the formation of CO_2, H_2, and various hydrocarbons the nature of which depends on many parameters such as the temperature, the nature of the starting cluster, the nature of the support, and, most important, its water content. There is no need for added hydrogen to carry out such reactions. We present here evidence to show that, upon heating a carbonyl cluster supported on alumina, the carbonyl ligands react with the hydroxyl groups (or adsorbed molecular water) of the support to produce H_2 and CO_2.[5] Furthermore, part of the H_2 produced by this reaction, or water from the support, reacts with the supported cluster to produce hydrocarbons either from carbonyl or from carbide thermally produced in the cluster cages.[6]

Thus in a typical experiment 200 mg of hydrated η-Al_2O_3 (315 m²/g) was carefully mixed under argon with 10 mg of carbonyl cluster complex. This supported cluster was placed in a glass reactor evacuated at room temperature for 1 h (10^{-5} Torr) and then heated at increasing temperature under argon. Whereas many hydrocarbons were observed at low temperature (T <200 °C), the selectivity toward methane reached 100% at 250 °C or above.

Table I indicates the mass balance between the CH_4 and CO_2 formed and the starting carbonyl ligands after all of the CO ligands have reacted (several hours at 300 °C for $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Rh_4(CO)_{12}$. $Rh_6(CO)_{16}$, and $Os_6(CO)_{18}$, and after several hours at 400 °C for $Os_3(CO)_{12}$). A blank experiment carried out using 200 mg of Al_2O_3 in the absence of a cluster complex gave no hydrocarbons or hydrogen and only traces of CO_2 (presumably physisorbed on the alumina surface). In the case of $Rh_6(CO)_{16}$, the hydrogen source was confirmed as the water on the alumina support by carrying out the reactions with an η-Al_2O_3 partially exchanged with deuterated water. In this case CD_4 was obtained with CD_3H, CD_2H_2, CDH_3, and CH_4 as well as with H_2, HD, and D_2 (mass spectroscopic analysis). We have not carried out an exact mass balance of hydrogen evolution to check if production of excess of hydrogen would define some oxidation of the noble metal cage, as was found for supported $Mo(CO)_6$.[7] However, in the case of $Rh_6(CO)_{16}$, the amount hydrogen (gaseous + hydrocarbon) produced was equivalent to the amount of carbon dioxide produced as expected from the stoichiometry of the water gas shift reaction.

Both thermogravimetric and infrared investigations on pure and supported cluster carbonyls[8] have shown that, below 250 °C, the total decomposition of the molecular clusters investigated here to metals is prevented and molecular cluster aggregates (of the original or different nuclearity) are still present. Only above 250 °C does a great deal of decomposition to metal take place, in parallel as expected with selective methanation of carbon monoxide.[9] In addition the reaction of CO with rhodium metal (prepared by H_2 reduction at 500 °C of $RhCl_3 \cdot 3H_2O$ (4% by weight) supported on η-alumina), even in the presence of added water, resulted only in traces of hydrocarbons at 250 °C.

The reactivity of the systems originated from the supported cluster complexes was estimated by the temperature at which a given amount of CH_4 was formed. The following order was

Table II. Product Distribution from the Reaction of 10 mg of Cluster Complex Supported on 200 mg of Al_2O_3 Heated under a Mixture of CO (380 Torr) and Argon (380 Torr)

Cluster	Temp, °C	Mol of CH_4/mol of cluster	Mol of CO_2/mol of cluster	(Mol of CH_4 + mol of CO_2)/mol of CO ligand	% convn (CO → CO_2)
$Ru_3(CO)_{12}$	300	5.8	42.1	4.0	55
$Os_3(CO)_{12}$	400	10.7	97.6	6.5	52
$Ir_4(CO)_{12}$	400	13.2	82.5	8.0	52
$Rh_6(CO)_{16}$	400	11.9	93.8	6.6	55
$Rh_4(CO)_{12}$	400	7.6	42.3	4.2	51
$Os_6(CO)_{18}$	400	13.3	85.7	5.5	47