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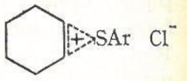

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remove radiation below 2200 Å. Bayes[1] found that the following mechanism described the photolysis with ethylene:

$$C_3O_2 + h\nu = :CCO + CO \qquad (1)$$

$$:CCO + C_2H_4 = CO + C_3H_4 \qquad (2)$$

$$:CCO + C_3O_2 = n CO + \text{polymer} \qquad (3)$$

The C_3H_4 was a mixture of allene and propyne, n was found to be 1. Assuming a steady concentration of :CCO and at low conversions,

$$(CO/C_3H_4) - 2 = 2(k_3/k_2)\,[C_3O_2]/[C_2H_4]$$

A plot of $[(CO/C_3H_4) - 2][C_2H_4]$ against $[C_3O_2]$ is a straight line through the origin of slope $2k_3/k_2$. For ethylene, Bayes found $k_3/k_2 = 1{\cdot}4$ against 1·3 in this work. The results in the table which are independent of pressure between 15 and 200 torr show that the reactivites of olefins with :CCO vary with structure in a way exactly opposite to that for other biradical species, for which similar data have been published. The variation is also different from that found with monoradicals. However, Frey[2] has found that CH_3CH:radicals produced from the photolysis of diazoethane react much faster with the C=C bond in propene than with either *cis*- or *trans*-but-2-enes. Also like :CCO radicals, ethylidene radicals show very little tendency to insert into a C–H bond.

Relative Reactivity of Olefins with Biradicals

Olefin	:CCO	Diene/Alkyne	$:CBr_2$	$:CCl_2$	:O	:S	:Se
Ethylene	1·00	3·7	—	—	1·00	1·00	1·00
Propene	0·313	12·8	—	—	5·8	3·6	2·6
But-l-ene	0·101	31·0	0·07[a]	0·023[a]	5·8	3·6	7·1
Isobutene	0·096	19·2	1·00	1·00	25·0	—	44·7
cis-But-2-ene	0·155	29·5	—	—	23·8	—	2·40
trans-But-2-ene	0·091	140	—	—	28·3	—	56·0
Trimethylethylene	0·040	45·0	3·20	2·90	79·3	—	—
Tetramethylethylene	0·020	∞	3·50	6·60	101·8	—	—
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The Structure and Photochemistry of Formaldazine

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A BRIEF REPORT[1] previously established the existence of formaldazine (I) and suggested that it had the cisoid form, unlike the similar conjugated molecules butadiene, glyoxal, and acraldehyde.[2] A re-examination of the infrared absorption of the gas (corroborated by spectra of the solid) has confirmed, by the activity both of four different fundamentals in the C–H bond-stretching region at 2943, 3007, 3078, and 3235 cm.$^{-1}$ and of the overtone of the intense 1019 cm.$^{-1}$-band at 2033 cm.$^{-1}$, that formaldazine indeed lacks a centre of symmetry. Further evidence is provided by the presence of a series of microwave transitions near 28,000 extending weakly to 29,800 Mc./sec., each

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line showing a second-order Stark effect (implying an asymmetric rotor).

Formaldazine has also been discovered to be formed in the reaction of methylene radicals with diazomethane both in solid films of the latter and in argon and nitrogen matrices at 20°K. The formaldazine is itself easily photolysed in both the inert matrix and an initially pure film of solid formaldazine, the products in both cases being methylenimine (III) and hydrogen cyanide, identified by their characteristic infrared absorption spectra. When gaseous formaldazine in a great excess of nitrogen is subjected to flash photolysis, a new transient pair of absorption bands, appearing immediately during the photolysis flash and decaying within 50 microseconds, are observed at 2808 Å (entirely diffuse) and 2847 Å (indications of structure); hydrogen cyanide and ammonia are prominent products (detected by infrared analysis) analogous to the methyl cyanide and ammonia found in the photolysis of acetaldazine.[3] The tentative assignment of these bands to the $H_2C{=}N\cdot$ free-radical can be made, the evidence of electron spin resonance spectra in argon matrices[4] confirming that this radical exists. The mechanism of the formation of the two products in the solids then involves the disproportionation of the methyleniminyl radicals (II) within the cage after severance of the weak N–N bond in the primary photochemical process:

$$\underset{\text{(I)}}{CH_2{=}N{-}N{=}CH_2} + h\nu \rightarrow \underset{\text{(II)}}{2CH_2{=}N\cdot}$$

$$\rightarrow \underset{\text{(III)}}{CH_2{=}NH} + HCN$$

Further details of these studies will be reported later.

I am indebted to Mr. M. C. L. Gerry for making the microwave measurements and to Mr. D. G. Horne for performing the flash photolysis experiments. I also thank Professor R. G. W. Norrish for his continued support and encouragement.

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The Attack of Methyl Radicals on Tetradeuterohydrazine

By PETER GRAY and A. JONES
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GRAY and THYNNE[1] recently reported values of the velocity constants for hydrogen abstraction from hydrazine by methyl radicals:

$$CH_3 + N_2H_4 \rightarrow CH_4 + \cdot NHNH_2$$

They found that hydrogen abstraction was rapid over the temperature range studied (110 to 180°C), and that temperature-dependence of the velocity constant corresponded to an activation energy E_H of $5{\cdot}0 \pm 0{\cdot}1$ kcal. mole^{-1} and a pre-exponential factor A_H of 10^{11} cm.^{3} mole^{-1}sec.$^{-1}$ The size of A is normal for hydrogen abstraction by methyl radicals and corresponds to a value for the 'steric factor' P defined by the equation $k = PZ\,exp(-E/RT)$ of *ca.* 10^{-3}, if the effective collision-diameters for methyl and hydrazine are assumed to be *ca.* 3·5 and 5 Å respectively.

We have now studied the abstraction of deuterium from N_2D_4 over the same temperature range using azomethane as the methyl radical source. The results can be fitted by the Arrhenius equation: (errors quoted are standard deviations of a least-mean-squares treatment): $\log_{10}\ (k_{N_2D_4}/\text{cm.}^3\text{mole}^{-1}\text{sec.}^{-1}) = (10{\cdot}86 \pm 0{\cdot}17) - (6390 \pm 320)/2{\cdot}303\ RT$. Since previous experiments in which hydrogen attached to nitrogen has been replaced by deuterium have shown that the activation energy for abstraction is generally increased by 1 to 2 kcal. mole^{-1}, the activation energy of 6·4 kcal. mole^{-1} found here substantiates the rather low value found for hydrazine. By combining the results for N_2H_4 and N_2D_4 it is possible to assess quantitatively the primary isotope effect due to substitution of D for H. At 150°C, the quotient (k_H/k_D) is $7{\cdot}0 \pm 0{\cdot}6$. The errors in the Arrhenius parameters are larger: the difference in activation energies, $(E_D - E_H)$ is $1{\cdot}4 \pm 0{\cdot}3$ kcal. mole^{-1} and $\log\ (A_D/A_H) = \bar{1}{\cdot}14 \pm 0{\cdot}18$, corresponding to $(A_D/A_H) = 0{\cdot}72$.

The simplest interpretation of kinetic isotope effects is based on the assumption that on passing from the reactants to the transition state the

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