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Reaction of Acetylene with Methyl Radicals

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CETYLENE will pyrolyze to benzene as a major A product at temperatures above 500°C; no appreciable pyrolysis reaction occurs below this temperature. We have generated methyl free radicals in the presence of acetylene at temperatures between 200 and 500°, and observe benzene as the major reaction product with propylene as the second most important product. Both mixtures of acetone- d_6 plus acetylene, and acetone plus acetylene- d_2 , (1:1 at total pressure of 100-200 mm Hg) were photolyzed with a medium pressure mercury arc. Under these conditions acetylene alone does not react to form any of the products noted in this Note. Products were separated by gas chromatography and characterized by mass spectrometer examination of the recovered fractions. Only 1 to 5% of the original material was allowed to react, and the separated compounds in the products were examined for deuterium content. A typical set of results is given in Table I. The data suggest a reaction mechanism in which a methyl radical adds to acetylene, and this radical then adds to another acetylene in a typical free radical initiated polymerization. When three acetylenes are added the radical is large enough so that intramolecular reaction occurs:

$$CD_3CHCHCHCHCHCHCH \rightarrow + CD_3.$$
 (1)

 \wedge

The benzene composition starting with normal acetylene is primarily d_0 , and starting with acetylene- d_2 is primarily d_6 in conformity with the proposed mechanism. In addition, some benzene may be formed by the $HC\equiv C$ radical adding two moles of acetylene and closing the ring to form a phenyl radical which stabilizes itself by abstraction.

The mechanism is further substantiated by the propylene. Propylene $(d_3 \text{ and } d_4)$ is a major product of the reaction of CD₃ radicals with acetylene, while propylene $(d_2 \text{ and } d_3)$ results from the reaction of CH₃ radicals with acetylene- d_2 . It is formed by addition of a methyl radical to acetylene

$$CD_3 + CHCH \rightarrow CD_3CH = CH$$
 (2)

and the stabilization of the resulting radical by abstraction of H or D from the parent compounds. Since the radical efficiently abstracts at temperatures as low as 250° it is not appreciably resonance stabilized. As an example, the resonance stabilized allyl radical will not abstract hydrogen until 420° .¹ We have not observed any pentadiene in the gas chromatogram of the products, but it might be buried under the acetone peak.

A polymer gradually builds up on the walls of the reaction vessel which chars when heated. The polymer probably accounts for the large deficiency of methyl radicals in the material balance of the gaseous phase. The polymer also is a clue to the efficient formation of carbon in acetylene diffusion flames and pyrolysis.

We have shown that benzene is one of the major products of the reaction of ethyl radicals and acetylene, so that homogeneous catalysis of acetylene to benzene by aliphatic free radicals is probably a general reaction.

Using CD_3 radicals it is possible to measure the relative rates of hydrogen abstraction from acetylene

TABLE I. Isotope distribution of the components and their percentage compositions in the photolysis of acetylene with acetone- d_6 and acetylene- d_2 with acetone.

Acetylene-Acetone- d_6 $T = 342^{\circ}$ C								
Fraction	Est. mole $\%$	$\% d_0$	$\% d_1$	$\% d_2$	$\% d_3$	$\% d_4$	$\% d_5$	% d
Methane	1.0			•••	43.1	56.9		
Acetylene	50.0	99.4	0.6	• • •				
Propylene	0.4		•••		43.0	55.0	1.0	0.3
Benzene	0.6	87.8	6.4	2.1	1.2	0.7	1.0	0.8
Toluene	Trace				primarily	• • •	• • •	• • •
Acetone-d ₆	43.0		• • •				• • •	• • •
Carbon monoxide	5.0		•••	•••	•••	•••	•••	
			Acetylene-d ₂ -a	cetone $T=2$	50°C			
Fraction		$\% d_0$	$\% d_1$	$\% d_2$	$\% d_3$	$\% d_4$	$\% d_5$	% d6
 Methane		87.0	13.0		•••			
Acetylene		0.5	3.8	93.7				
Propylene				93.0	7.0			
Benzene							9.0	91.0

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versus deuterium abstraction from acetone- d_6 by measuring the isotope composition of the methanes:

$$CD_{3} + C_{2}H_{z} \rightarrow HC \equiv C + CD_{3}H$$
(3)

$$CD_3 + (CD_3)_2CO \rightarrow CD_2COCD_3 + CD_4.$$
 (4)

A measure of log CD₃H/CD₄ versus $1/T^{\circ}$ K gives the energy of activation difference between (3) and (4). The E_{act} for CD₃ abstracting D from acetone- d_6 has been independently determined.² With this information we have determined the activation energy for (3) to be 14 kcal per mole. We have also determined that the E_{act} for abstracting deuterium from C₂D₂ with CH₃ radicals is 18.4 kcal/mole.

¹ J. R. McNesby and A. S. Gordon, J. Am. Chem. Soc. **79**, 4593 (1957). ² E. Whittle and E. W. R. Steacie, J. Chem. Phys. **21**, 993

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Rotational Transfer in the Fluorescence Spectrum of $OH(2\Sigma^+)^*$

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THE data presently available on the transfer be-L tween rotational and translational energy have been summarized by McCoubrey and McGrath.¹ Data obtained from experiments on the dispersion and absorption of sound, heat capacity lag in gas dynamics, and measurements of the thickness of shock fronts are in fair agreement that for many diatomic molecules other than hydrogen and hydrides, the number of collisions required for rotational relaxation is in the range 5-20. For hydrogen the number of collisions is of the order 300. The results are usually obtained as a single average relaxation time for the adjustment of a Boltzmann distribution from one temperature to another. Experimental information on the probability of collisions leading to transfer between arbitrary rotational states is not available.

Attempts to use spectroscopic methods to study collisional transfer of energy between molecules generally meet with the following difficulty. When one observes the effects of a change in external parameters of the system, such as pressure, temperature, or gas composition, on the distribution of molecules in the emitting levels, it is usually not possible to determine whether the change in distribution is due to the effect of experimental conditions on the excitation process, or on the subsequent energy transfer processes



FIG. 1. Steady-state rotational distribution in the F_2 levels (filled circles) and F_1 levels (open circles) of the vibrational ground state of OH($^{2}\Sigma^{+}$) when level K=11, $J=10\frac{1}{2}$ is excited. The effect of a small amount of absorption populating the level K=10 has been subtracted, along with the contributions of thermal emission and scattered light. The corresponding calculated equilibrium distribution of the same number of molecules at 1300° K is shown for comparison. This is the observed rotational temperature in the electronic ground state. The rotational distribution in the excited state in the absence of the bismuth radiation is not known since the very weak emission is obscured by light scattered from the reaction zone.

by which the initial nonequilibrium distribution approaches equilibrium. Spectroscopic studies of discharges and flames are particularly subject to this difficulty in interpretation.²

This letter describes a method capable of giving the probability of collisional transfer between specific rotational levels, under conditions where the nature of the excitation mechanism and its dependence on the conditions of the experiment are unambiguously known. OH molecules in the burnt gases[†] (about 1300°K) above an acetylene-oxygen flame burning at 3 mm pressure are excited to the state with rotational angular momentum quantum number K=11, having total angular momentum $J = K - \frac{1}{2}$, in the lowest vibrational level of the ${}^{2}\Sigma^{+}$ electronic state. This excitation is produced by absorption of the strong bismuth resonance line 3067.7 A, which coincides with the R₂10 line of OH.[‡] The bismuth line is obtained from a sealed discharge tube containing BiCl3 and argon at 5 mm Hg pressure, excited by a 2450 Mc diathermy unit. The relative populations of the initial OH rotational state and of other states populated by collisions