The Chemistry of Singlet and Triplet C_2 Molecules

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Summary Diatomic carbon reacts with acetone to form acetylene by two different mechanistic pathways: one of which exhibits radical character and one which is indiscriminant.

IN the course of examining the deoxygenation of carbonyl compounds[1] it was observed, using carbon-14 labelling, that the C_2 molecule reacted with acetone to give acetylene. When a mixture of 55·3 mole % $[^2H_0]$acetone and 44·7 mole % $[^2H_6]$acetone was used as the reactive matrix for C_2 the composition of the recovered acetylene was analysed by low-voltage mass spectroscopy and exhibited the following composition: C_2H_2 (51·0%), C_2HD (12·3%), and C_2D_2 (36·7%). Using twice the amount of C_2HD as a measure of the intermolecularity of the reaction it is seen that the reaction of C_2 with acetone to form acetylene is 25% intermolecular and 75% intramolecular. The observation of an intermolecular acetylene-forming pathway was consistent with the intermediacy of an ethynyl radical. It also appeared reasonable that the precursor of an ethynyl radical would be the triplet C_2 molecule. This assumption was supported by the fact that the metastable triplet $(X'^3\Pi_u)$ of C_2 is known to be only 0·075 ev above the singlet $(X^1\Sigma_g^+)$ ground state.[2] Since the C_2 molecules require *ca.* 10^{-5} s to reach the liquid-nitrogen-cooled reaction zone,[3] the singlet ground state and the long-lived triplet should be the only species present at the time of reaction as upper states would have decayed to one of these two states. Therefore, if the triplet were responsible for the intermolecular reaction, the intramolecular reaction could be assigned to the singlet ground state reacting by a process leading directly to acetylene or possibly through a vinylidene species.

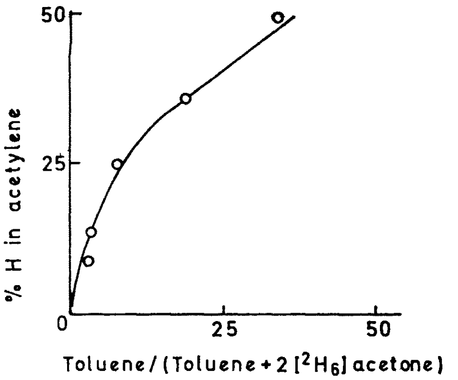
$$(CH_3)_2C{=}O + \cdot C{\equiv}C\cdot \rightarrow HC{\equiv}C \rightarrow HC{\equiv}CH$$

$$\begin{tikzcd}(CH_3)_2C{=}O + C_2 \arrow[r] \arrow[d] & C_2H_2 \\ {[H_2C{=}C{:}]} \arrow[ur, "\sim H"'] & \end{tikzcd}$$

In matrix trapping of C_2 with CH_3CHO–CD_3CDO and

C_6H_6–C_6D_6 mixtures, the intermolecularities of acetylene formation are 29 and 18%, respectively. The presence of two pathways in the structurally different systems, strengthens the hypothesis of two reactants.

The presence of an intermolecular pathway for acetylene formation suggested that the intermediates involved had considerable mobility in the matrix. If this were the case and ethynyl radicals were involved, a selectivity in hydrogen atom abstraction would be expected, since Gunning and Strausz have shown[4] that ethynyl radicals from the photolysis of bromoacetylene–nitric oxide mixtures display a selectivity similar to a chlorine atom. This hypothesis was tested by preparing mixtures of [$^2H_6$]acetone and small quantities of hydrogen-containing compounds having carbon–hydrogen bonds of varying strength and measuring the amount of hydrogen incorporation into the acetylene as a function of the strength of the weakest carbon–hydrogen bond in the doping molecule. The presence of small amounts of added impurity in the matrix did not disturb the overall yield of acetylene, which was *ca.* 75% based on the C_2 available for reaction.



FIGURE

The first mixed matrix consisted of 87 mole % [$^2H_6$]-acetone and 13 mole % [$^2H_0$]chloroform. Since chloroform has a carbon–hydrogen bond of 93[5] and the acetone 92 kcal/mole,[6] the incorporation of hydrogen into the acetylene should be nearly statistical. The measured hydrogen incorporation in the acetylene was 5·5%, indicative of no appreciable selectivity since, by the suggested mechanism, the intramolecular pathway cannot be operative with chloroform to give [$^2H_0$]acetylene. However, if the reactive matrix contains 92 mole% [$^2H_6$]acetone and 8 mole% [$^2H_0$]acetaldehyde the recovered acetylene contained 21 mole% hydrogen, reflecting a much higher than statistical hydrogen incorporation. We attribute this high incorporation to the weak, acyl carbon–hydrogen bond (78 kcal/mole)[7] and its high reactivity as a hydrogen atom donor in free-radical reactions.[8] That the enhancement of hydrogen incorporation is due to the acyl hydrogen rather than the α-hydrogens of the acetaldehyde was confirmed by using a matrix of 5 mole% CH_3CDO in $(CD_3)_2CO$, which led to a hydrogen incorporation of only 3 mole% in the recovered acetylene.

When [$^2H_6$]acetone and [$^2H_0$]toluene, which has benzylic hydrogens with a bond strength of 83 kcal/mole,[9] are used in varying compositions as the reactive matrix for C_2, a plot of the mole% hydrogen incorporation into the acetylene against the "mole fraction of CH_3 groups" $CH_3/(CH_3 + CD_3)$ is nonlinear, as shown in the Figure. It should be noted that the prominent change of slope in the Figure is consistent with two different pathways to acetylene. Superimposed on the non-selective formation of C_2H_2 and C_2D_2 from singlet C_2 is the reaction of the triplet, $C_2 \rightarrow C_2H \rightarrow C_2H_2$, which shows a high degree of preference for toluene.

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