Communication: The Reactions of c-C_3H_5 Radicals with HCN and ClC_6H_5 in CCl_4

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Current knowledge about the c-C_3H_5 radical has been summarized by Walborsky [1]. The relative reactivities of quite a variety of molecules toward c-C_3H_5 have been measured, e.g., olefins [2], aromatics [3,4], and tetrahalogenated methanes [5] and it has been concluded [1] that "the c-C_3H_5 radical behaves as a rapidly inverting σ radical of high reactivity and low nucleophilicity."

We have determined the reactivity of these radicals toward non-saturated compounds such as HCN with a triple $C \equiv N$ bond and an aromatic compound, chlorobenzene, in both cases relative to the abstraction reaction of Cl atom from the solvent, CCl_4.

Cyclopropyl radicals were generated by thermal decomposition of *bis*(cyclopropylformyl) peroxide (I). At first several experiments were done with solutions of (I) 1.0×10^{-2} M and 2.5×10^{-2} M in CCl_4. In a general procedure, ampoules of 10 cm^3 in volume were filled with these solutions and attached to a conventional grease-free high vacuum line and the sample degassed several times before sealing off under vacuum. The ampoule was then immersed in a thermostatted water bath at 64°C for a period of time long enough to ensure that the decomposition of (I) was not greater than 10% after which is was transferred to a flask cooled in liquid nitrogen and the reaction quenched. The ampoule was then attached to the vacuum line and its content transferred via a break-seal to a glass bulb. The products, volatile at -40°C, were collected for gas chromatographic analysis in addition to other less volatile products which were expelled from the solution by N_2 bubbling and stirring to ensure quantitative recollection.

The products found by gas chromatography on a 6-m dinonyl phthlate column at 60°C using a thermal conductivity detector as well as infrared and mass spectrometry were CO_2, c-C_3H_6, c-ClC_3H_5, and C_2Cl_6.

The thermal decomposition of (I) in CCl_4 solution has been studied by Hart and Wyman [6]. At variance with these authors, we have not found among the products, despite exhaustive search, cyclopropyl cyclopropanecarboxylate or cyclopropyl-carboxylic acid possibly due to the low conversion at which our experiments were carried out. Under these conditions we can assess:

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International Journal of Chemical Kinetics, Vol. 25, 63–66 (1993)

CCC 0538-8066/93/010063-04

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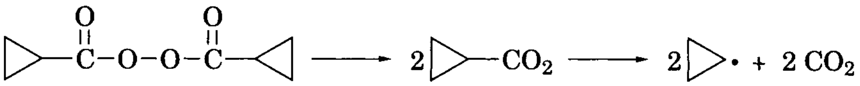

(I)

and the mass balance:

$$n_{CO_2} = n_{c\text{-}C_3H_6} + n_{c\text{-}ClC_3H_5} \tag{2}$$

with an error of ±0.2% was verified.

c-ClC_3H_5 is formed from the abstraction reaction of Cl from the solvent:

$$c\text{-}C_3H_5 + CCl_4 \xrightarrow{k_{Cl}} c\text{-}ClC_3H_5 + CCl_3 \tag{3}$$

and the abstraction reaction of H from (I) by c-C_3H_5 would account for the formation of c-C_3H_6.

In the presence of HCN, under the same experimental conditions, the yields of c-C_3H_6 and c-ClC_3H_5 decrease. This could be attributed to the addition reaction of c-C_3H_5 to the triple bond to form an adduct radical:

$$c\text{-}C_3H_5 + HCN \xrightarrow{k_{add}} \text{Add.} \tag{4}$$

which in turn would give an imine, since mass spectral peaks at m/e > 150 are present in experiments with HCN and it is well known that in the liquid phase most imines of small molecular size are unstable and polymerize readily [7].

Hence, the rate of addition of the c-C_3H_5 radical relative to the abstraction reaction of Cl atom from CCl_4 is given by:

$$\frac{R_{add}}{R_{c\text{-}ClC_3H_5}} = \frac{k_{add}\, X_{HCN}}{k_{Cl}\, X_{CCl_4}} \tag{5}$$

with X = molar fraction; R_{add} = rate of addition, and $R_{c\text{-}ClC_3H_5}$ = rate of formation of c-ClC_3H_5.

R_{add} can be calculated from the "missing" c-C_3H_5 radicals so that:

$$R_{add} = R_{CO_2} - R_{c\text{-}C_3H_6} - R_{c\text{-}ClC_3H_5}$$

if the adduct formed by the addition reaction does not further react with another c-C_3H_5 radical. The ratio of molar fractions, X_{HCN}/X_{CCl_4}, was varied by a factor of 4 and eq. (5) is correctly verified as seen in Figure 1.

Similar experiments were performed with ClC_6H_5 as the substrate. In this case $X_{ClC_6H_5}$ was varied between 0.1 and 0.5. Product analysis revealed the presence of CO_2, c-C_3H_6, c-ClC_3H_5, and C_2Cl_6, as in the blank experiments, in addition to *o*-*m*- and *p*-chlorocyclopropylbenzene identified by gas chromatography on a DC silicon grease column, infrared [8] and mass spectrometry [9].

For the reaction of c-C_3H_5 with HCN, k_{add}/k_{Cl} does not vary significantly with temperature in the range 50–70°C. At 64°C $k_{add}/k_{Cl} = 11.4 \pm 0.9$. For the reaction of c-C_3H_5 with ClC_6H_5, $k_{add}/k_{Cl} = 1.5 \pm 0.5$ at the same temperature. An estimation of the absolute rate constants for the addition reactions could be made using the value of the rate constant for the Cl-

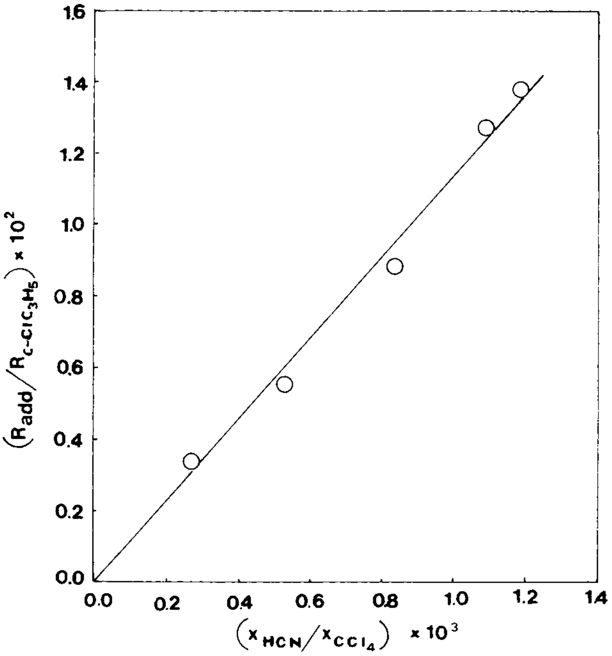

Figure 1. Rate of addition of c-C_3H_5 radicals to HCN relative to the rate of formation of c-ClC_3H_5 vs. the ratio of molar fractions at 64°C.

abstraction reaction from CCl_4 by c-C_3H_5 radicals given by Johnston et al. [4] who studied the temperature dependence of the kinetics of this reaction between 0 and 68°C in a mixture of 1 : 4 benzene : $CF_2ClCFCl_2$.

The higher reactivity of the c-C_3H_5 radical toward HCN would correlate with a higher ionization potential of HCN (13.7 eV) compared with ClC_6H_5 (9.07 eV) [10]. This same trend has been observed previously for the rates of addition of c-C_3H_5 radicals to olefins [2]. Further work on this subject is being carried out.

Acknowledgment

We acknowledge support from CONICET and CONICOR, Argentina.

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Received April 29, 1992
Accepted August 14, 1992