Thermally Initiated Free-Radical Chain Addition of Alkanes to Alkynes, II[1]

Kinetics of the Addition of Cyclohexane to Phenylethyne under Supercritical Fluid Conditions

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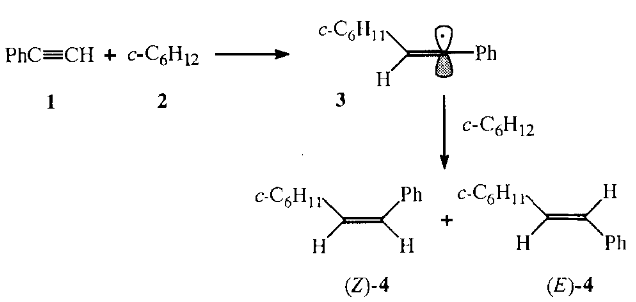
The kinetics of the addition of cyclohexane (**2**) to phenylethyne (**1**) proceeding via 2-cyclohexyl-1-phenylethenyl radical (**3**) to give 1-cyclohexyl-2-phenylethene (**4**) was investigated in the temperature range from 260 to 340°C. The radical chain is initiated by a bimolecular reaction of cyclohexane with phenylethyne to give a cyclohexyl radical and a 1-phenylethenyl radical. The physical state of the reaction mixture was varied from liquid to supercritical and to gas-phase conditions. No effect on the reaction rate constant near the critical point was observed.

Alkanes can be added to alkenes in a thermally initiated free radical chain reaction (ane reaction)[2,3]. The radical chain is initiated by a molecule-induced homolysis of alkane and alkene to give two alkyl radicals[4].

$$R{-}H + H_2C{=}CHX \rightleftharpoons R^{\bullet} + H_3C{-}\dot{C}HX$$

The ane reaction can also be applied alkynes[1,5]. We have shown that the ane reaction is suitable to study the stereoselectivity of free radical additions of cyclohexane to 1-alkynes via 1-alkenyl radicals to give 1,2-disubstituted alkenes[1,6]. We have now studied the kinetics of the thermally initiated free radical chain addition reaction of phenylethyne (**1**) to cyclohexane (**2**) proceeding via 2-cyclohexyl-1-phenylethenyl radical (**3**) to give 1-cyclohexyl-2-phenylethene (**4**) in the temperature range from 260 to 340°C, varying the state of the reaction mixture from liquid to supercritical fluid and then to gas-phase conditions. The critical data of cyclohexane are: T_c 280.4; p_c 40.7 bar; ρ_c 0.273 g·cm^{-3} [7]. Our goal was to find out whether the reaction sequence would be analogous to the respective reaction of alkenes and alkanes and whether there could be observed any effect on the reaction rate constant near the critical point[8].



Results

Cyclohexane (**2**) was allowed to react in the absence of air with alkyne **1** (ratio 1000:1) in a high-pressure high-temperature flow apparatus[2,9] in the temperature range from 260 to 340°C. The samples were analyzed by quantitative GC. The conversion of **1** and the formation of the addition products **4** at 340°C and 200 bar are shown in Figure 1.

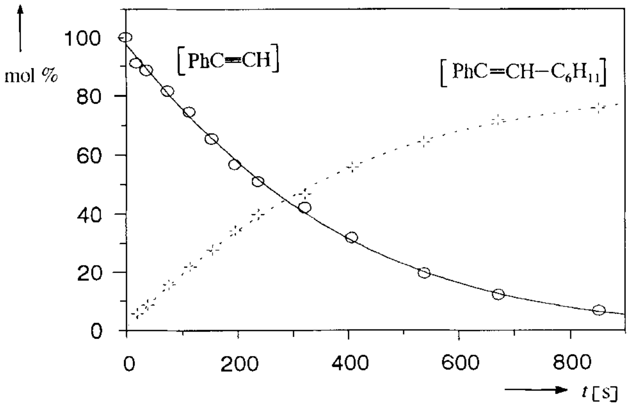


Figure 1. Conversion of phenylethyne (**1**) and formation of the addition products **4** [Σ(*Z*)-**4**, (*E*)-**4**] at 340°C and 200 bar (5.82 M cyclohexane)

The conversion of alkyne **1** was approximately 90% after a reaction time of 10 min, and 80% of the product **4** was formed. The ratio of the stereoisomers was [(*Z*)-**4**]:[(*E*)-**4**] = 0.47 and 0.45 at a conversion of 10 and 90%, respectively. Thus, only minor (*Z*) to (*E*) isomerization of the addition products under the reaction conditions was observed. Some minor products such as regioisomeric products were also formed. By a variation of the concentration of **1** from 4 to

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14 mmol·l^{-1} at 320°C the rection was shown to be first order with respect to ethyne **1** (Table 1, entries 7, 15, 16). Figure 2 gives the pseudo-first-order plots of the conversion of ethyne **1** in the range from 260 to 340°C. A linear correlation is obtained up to approximately 50% conversion. However, the reaction rate is enhanced with increasing conversion of **1**. The Arrhenius plot of the pseudo-first-order rate constants k' gives a good linear correlation with an activation energy of 89 kJ/mol and lg A = 5.1 s^{-1} (Figure 3). The reaction is first order in cyclohexane as shown by independent measurements. Thus, the concentration of cyclohexane was varied at 280 and 320°C by a variation of the pressure from undercritical to supercritical conditions. The results are given in Table 1 (entries 3, 10, 11 and 7, 12, 13, 14, respectively). The dependence of the concentration of cyclohexane on temperature and pressure is reported in ref.[10].

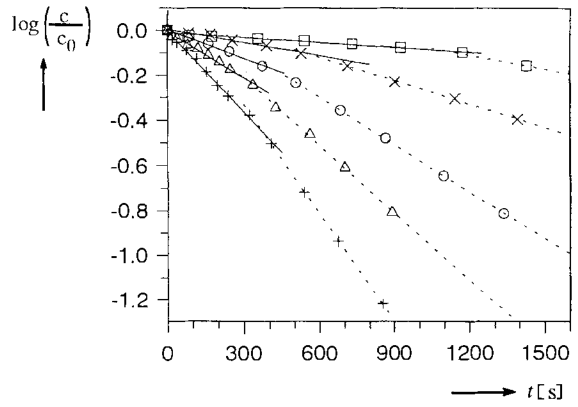

Figure 2. Addition of cyclohexane to phenylethyne (**1**). Conversion of **1** (pseudo first order) at a pressure of 200 bar. Variation of temperature (□: 260°C, ×: 280°C; ○: 300°C, Δ: 320°C, +: 340°C)

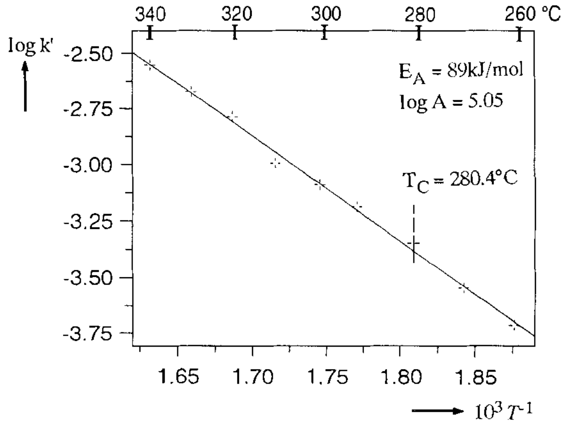

Figure 3. Temperature dependence of the pseudo-first-order rate constant of the addition of cyclohexane to phenylethyne (**1**) (Arrhenius plot)

Table 1. Pseudo-first-order rate constants $k'_{\text{exp.}}$ and derived rate constants k of the addition of cyclohexane (**2**) to phenylethyne (**1**) and concentrations of **1** and **2** under the reaction conditions

No.	T [°C]	p [bar]	**1** [M]	**2** [M]	$k'_{\text{exp.}} \cdot 10^4$ [s^{-1}]	$k \cdot 10^5$ [M^{-1} s^{-1}]
1	260	200	0.00855	6.89	1.96	2.84
2	270	200	0.00798	6.75	2.88	4.27
3	280	200	0.00818	6.62	4.26	6.43
4	290	200	0.00801	6.49	6.58	10.1
5	300	200	0.00752	6.36	8.22	12.9
6	310	200	0.0074	6.23	10.2	16.4
7	320	200	0.0075	6.09	16.4	26.9
8	330	200	0.00737	5.96	21.2	35.6
9	340	200	0.0072	5.82	28.1	48.3
10	280	80	0.00713	5.75	2.88	5.01
11	280	40	0.0051	3.24	1.78	5.50
12	320	100	0.0066	5.06	11.5	22.7
13	320	60	0.00442	3.10	6.02	19.4
14	320	30	0.00135	0.81	2.00	24.7
15	320	200	0.00441	6.08	14.8	24.3
16	320	200	0.0139	6.08	14.9	24.5

The experimental results can be described by equations (1) and (2).

$$-\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = k'[\mathbf{1}] = k\{\mathbf{1}][\mathbf{2}] \tag{1}$$

$$\lg k[\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}] = 4.8 - 95.000/19.15\cdot T \tag{2}$$

Discussion

The experimental kinetic results can be described by a free radical chain reaction analogous to the addition of alkanes to alkenes[2,3]. The radical chain is initiated by a bimolecular reaction of cyclohexane (**2**) with alkyne **1** to give cyclohexyl radical (**5**) and 1-phenylethenyl radical (**6**). The latter radical abstracts hydrogen from the solvent cyclohexane to give another radical **5**. Radical **5** adds to alkyne **1** to give radical **3**. However, in contrast to the reversible addition of radical **5** to alkenes at elevated temperature[2,3], the addition of **5** to alkyne **1** seems to be irreversible under the reaction conditions. Hydrogen transfer from cyclohexane to radical **3** yields the stereoisomeric addition products (Z)-**4** and (E)-**4**. The radical chain is terminated by a bimolecular reaction of radical **5** with alkenyl radical **3**.

$$\mathbf{1} + \mathbf{2} \overset{k_i}{\rightleftharpoons} \underset{\mathbf{5}}{c\text{-}\mathrm{C_6H_{11}^{\bullet}}} + \underset{\mathbf{6}}{\mathrm{Ph\dot{C}{=}CH_2}}$$

$$\mathbf{2} + \mathbf{6} \longrightarrow \mathrm{PhCH{=}CH_2} + \mathbf{5}$$

$$\mathbf{1} + \mathbf{5} \xrightarrow{k_A} \mathbf{3}$$

$$\mathbf{2} + \mathbf{3} \xrightarrow{k_H} \mathbf{4} + \mathbf{5}$$

$$\mathbf{5} + \mathbf{3} \xrightarrow{k_t} \text{chain termination}$$

Application of the quasistationary principle gives equations (3) and (4) and finally (5) with $k_{\mathrm{H}}[\mathbf{2}] \gg k_t[\mathbf{5}]$.

$$[\mathbf{5}] = \frac{k_i[\mathbf{1}][\mathbf{2}]}{k_t[\mathbf{3}]} \tag{3}$$

$$\frac{\mathrm{d}[\mathbf{3}]}{\mathrm{d}t} = k_\mathrm{A}[\mathbf{1}][\mathbf{5}] - k_\mathrm{H}[\mathbf{2}][\mathbf{3}] - k_t[\mathbf{5}][\mathbf{3}] = 0 \tag{4}$$

$$[\mathbf{3}] = \frac{k_\mathrm{A}[\mathbf{1}][\mathbf{5}]}{k_\mathrm{H}[\mathbf{2}]} = \frac{k_\mathrm{A}^{1/2}(k_i/k_t)^{1/2}[\mathbf{1}]}{k_\mathrm{H}^{1/2}} \tag{5}$$

The reaction rate of the formation of product **4** is given by equation (6). By insertion of equation (5) into (6) equation (7) is obtained.

$$\frac{d[\mathbf{4}]}{\mathrm{d}t} = k_\mathrm{H}[\mathbf{2}][\mathbf{3}] \tag{6}$$

$$\frac{\mathrm{d}[\mathbf{4}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = k_\mathrm{H}^{1/2} \cdot k_\mathrm{A}^{1/2}(k_i/k_t)^{1/2}[\mathbf{1}][\mathbf{2}] \tag{7}$$

Equation (7) is identical with the experimental rate law (1). The experimental pseudo-first-order rate constant k' is given by equation (8).

$$k' = k_\mathrm{H}^{1/2} \cdot k_\mathrm{A}^{1/2}(k_i/k_t)^{1/2}[\mathbf{2}] \tag{8}$$

The addition products **4** can also initiate the free radical chain by molecule-induced homolysis. This initiation reaction should be faster than the initiation reaction of alkyne **1** with cyclohexane because of the formation of a stabilized benzyl radical. That could explain the observed enhancement of the reaction rate after a conversion of approximately 50% of alkyne **1** (Figure 2).

$$\underset{\mathbf{4}}{\mathrm{PhCH{=}CHC_6H_{11}}} + c\text{-}\mathrm{C_6H_{12}} \xrightarrow{k_i'} \mathrm{Ph\dot{C}H{-}CH_2C_6H_{11}} - c\text{-}\mathrm{\dot{C}_6H_{11}}$$

There has been a discussion in the literature, if changes in solvent properties near the critical point may influence reaction rates[8]. As can be seen from Figure 3 and the results given in Table 1, no influence of the physical state of the reaction mixture and of the properties of the solvent near the critical point could be observed in the investigated free-radical-chain reaction[11].

In conclusion our results show that

1. alkanes can be added to alkynes in a thermally initiated free radical chain reaction;
2. the radical chain is initiated by a bimolecular reaction of alkane with alkyne to give an alkyl radical and an alkenyl radical;
3. the reaction rate is enhanced by an additional initiation reaction: the molecule-induced homolysis of the formed alkene **4** and cyclohexane;
4. the addition of cyclohexyl radical to phenylethyne seems to be irreversible under the reaction conditions;
5. no effect on the reaction rate constant could be observed near the critical point.

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Experimental

Analytical GC: Carlo Erba HRGC 5300 with FID detector and Spectra Physics Data Jet Integrator, fused silica capillary column DB1 30 m. Phenylethyne (**1**) (Janssen) was purified by Spaltrohr distillation. Cyclohexane p.A. (Riedel-de Haën) was freshly distilled. The addition products (*E*)- and (*Z*)-1-cyclohexyl-2-phenylethene (**4**) were independently synthesized as described in ref.[1].

Kinetic Measurements were carried out by using a high-pressure high-temperature flow apparatus as described in ref.[2,3]. 40 ml of a deoxygenated solution of phenylethyne in cyclohexane (≈0.01 M) with *n*-decane as internal standard was used under N_2 to carry out the reaction. The samples were analzyed directly by GC. In addition, 0.005 M and 0.02 M solutions were allowed to react at 320°C to determine the reaction order with respect to phenylethyne. The results are given in Table 1, Figures 1 and 2.

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