Investigation of the Reaction of Naphthalene with $O(^3P)$ in the Gas Phase

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The rate of the reaction between naphthalene and atomic oxygen in the electronic ground state was determined in a discharge flow system with mass spectrometric detection for temperatures between 362 and 773 K. All measurements were performed in an excess of O atoms over hydrocarbon. The second order rate constant was determined to be

$$k(T) = (1.14 \pm 0.87) \cdot 10^{13} \exp\left(-\frac{909 \pm 196}{T/\mathrm{K}}\right) \mathrm{cm^3\,mol^{-1}\,s^{-1}}.$$

Kinetic data are compared with data about the reactions of other aromatic substances and atomic oxygen in the ground state. Some possible reaction channels are discussed.

1. Introduction

Naphthalene is a widely used substance of technical interest, and it often occurs in combustion processes and flames in rich mixtures. In recent papers [1–4] kinetic data about the reactions of aromatic hydrocarbons with $O(^3P)$ in the gas phase have been reported. Naphthalene is the first polyaromatic hydrocarbon of which we investigated the reaction with atomic oxygen.

2. Experimental

The apparatus is described elsewhere [3, 4], so that only a short summary is given.

The measurements were performed in a low-pressure discharge flow system with molecular beam sampling and mass spectrometric analysis of reactants and products at pressures between 1.7 and 3.4 mbar and temperatures between 362 and 773 K. O atoms were produced by microwave discharge in O_2/He-mixtures. The He/hydrocarbon-mixture was injected into the system by a moveable probe.

The purity of naphthalene was >99% (Fluka). It was low temperature vacuum destilled for further purification. The purity of the gases was >99.99% (Messer-Griesheim).

3. Results

As mentioned above, the kinetic measurements were performed in an excess of O atom concentration over naphthalene concentration. The excess-ratio varied between 45 and 1070 so that the reaction took place under first-order conditions:

$$\frac{\mathrm{d}\,[\mathrm{HC}]}{\mathrm{d}t} = -k_{\mathrm{exp}}\,[\mathrm{HC}],$$

where [HC] stands for hydrocarbon concentration.

The reaction between naphthalene and O atoms was observed via the parent peak $m/e = 128$ of naphthalene. The temperature and pressure ranges are given above. The reaction was observed to be pressure-independent in this range.

Figure 1 shows the Arrhenius plot; its corresponding Arrhenius expression is

$$k(T) = (1.14 \pm 0.87) \cdot 10^{13} \cdot \exp\left(-\frac{909 \pm 196}{T/\mathrm{K}}\right) \mathrm{cm^3\,mol^{-1}\,s^{-1}}.$$

The activation energy for this reaction is (7.6 ± 1.6) kJ $\mathrm{mol^{-1}}$ in the temperature range up to 700 K.

4. Discussion

Figure 2 shows the enthalpies for the educts and some products at 298 K. Following the electrophilic addition of the O atom to the aromatic ring the resulting triplet biradical may stabilize to α- or β-naphthol.

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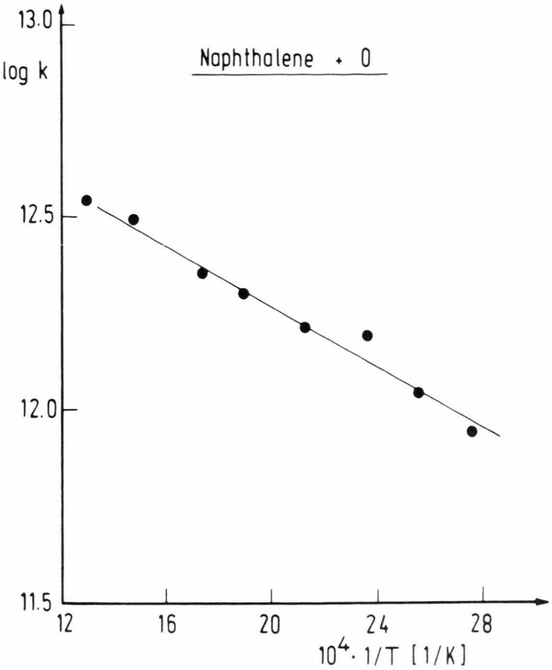

Fig. 1. Arrhenius plot for the reaction of naphthalene + O(^{3}P).

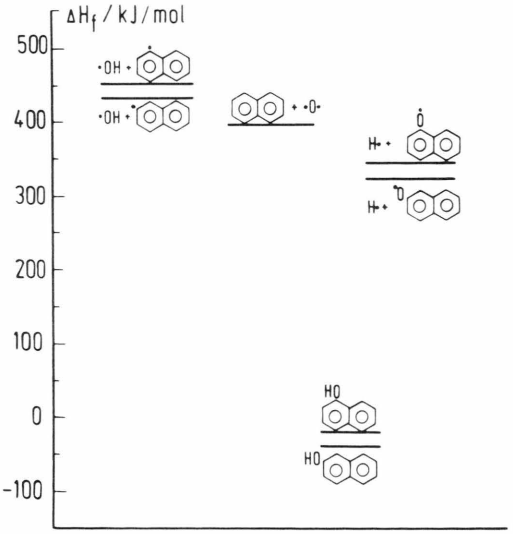

Fig. 2. Heats of formation for the educts and some products of the reaction between naphthalene and O(^{3}P). Data from [12] and [13].

Product analysis gave a signal at $m/e = 144$ which may be naphthol. Distinction between the two isomers was impossible. An analogous observation was made by Zadok et al. [5], who investigated the reaction in the liquid phase at 278 K and detected as main products α- and β-napthol in the ratio 7 : 1. Another exothermic reaction channel would be the elimination of an H atom of the triplet biradical under formation of naphthoxy radicals. Corresponding signals could not be detected. Because of the endothermicity of the reaction also H abstraction from naphthalene to form naphthyl and OH radicals is less probable.

As can be seen in the recent compilation of Cvetanovic [6], there are no other data about kinetic measurements of the reactions of O atoms with naphthalene available. The evaluated activation energy of 7.6 kJ/mol is unusually low compared to those for the reactions of other aromatic hydrocarbons with O atoms [6, 1–4]. Leidreiter [7] investigated the reaction of benzene and O(^{3}P) in a shock tube and confirmed an activation energy of 19.5 kJ/mol. It is therefore 2.5 times higher than the one for naphthalene and O atoms, while the preexponential factors for both reactions are fairly equal. A similar observation has been made by Mani and Sauer [8] for the reaction of H atoms with naphthalene, which is also much faster than the analogous reaction with benzene. The low activation energy for the naphthalene reactions may be explained by the particular structure of this annelated system. Naphthalene is well known to react faster than the monocyclic aromatic hydrocarbons. According to Clar [9], the two circles in the formula for naphthalene stand for six and four π-electrons in the different rings. In a monocyclic system the aromatic sextett symbolizes six π-electrons representing the typical aromatic, or better, benzenoid stability.

If the sextett is shared among more rings the benzene-like character is "diluted". This must necessarily lead to a gradual loss of benzenoid character and to a rapid increase in the reactivity in the acene series from benzene to naphthalene and further to the system with three annelated rings (anthracene).

Actually, ^{1}H-NMR-spectra do not verify Clar's model exactly but nevertheless it gives a good correlation for the various compounds [10].

As the reactions of O atoms with aromatics are considered to be electrophilic [6] a plot of the evaluated activation energies vs. ionization potentials should be linear. According to the ionization potential decrease from benzene (9.25 eV) to anthracene (7.85 eV) the latter is expected to have an activation energy of about 1.5–2.5 kJ/mol for the reaction with O atoms. This is also in accordance to Price [11], who calculated increasing charge densities in the series benzene, naphthalene and anthracene which simplify an electrophilic attack in this order.

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