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A cw Laser Absorption Study of the Reactions of Phenyl Radicals with NO, NO₂, O₂ and Selected Organics Between 298-404 K

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Rate constant for the reactions of phenyl (C_6H_5) radicals with NO, NO₂, O₂, C₂H₄, 2-butene, benzene, toluene and CCl₄ have been determined using a combined laser photolysis/laser absorption technique. Phenyl radicals were generated by 248 nm excimer laser photolysis of C₆H₅X, where X = Cl, Br and NO. Their temporal behaviour was monitored using cw-laser line absorption in the $\tilde{X}^2A_1 - \tilde{A}^2B_1$ transition at 488 nm. At this wavelength the absorption cross section of phenyl has been determined as (9 ± 4) 10⁻¹⁹ cm². For the rate coefficients of reaction with (1) NO, (2) NO₂ and (3) O₂ in the temperature range 298-404 K the following expressions were obtained.

 $k_1 = (4.0 \pm \frac{3.8}{1.5}) \ 10^{-12} \exp \left[(300 \pm 100)/T \right] \text{ cm}^3/\text{s}$ $k_2 = (1.3 \pm \frac{3.8}{2.3}) \ 10^{-12} \exp \left[(540 \pm 180)/T \right] \text{ cm}^3/\text{s}$ $k_3 \le 2 \cdot 10^{-17} \text{ cm}^3/\text{s}$

The magnitude of the rate coefficients k_1 and k_2 and their negative temperature dependence suggest that the reactions between phenyl and NO/NO₂ occur as radical recombination and/or (in the case of NO₂) as O-atom metathesis reaction. The apparent low reactivity of phenyl with O₂ is likely to be caused by insufficient thermal stability of the phenylperoxi radical. For the reactions of phenyl with selected organics the following upper limits of the rate coefficient at 298 K were determined: k_4 (C₂H₄) $\leq 8 \cdot 10^{-17}$ cm³/s; k_5 (C₂H₂) $\leq 8 \cdot 10^{-16}$ cm³/s; k_6 (2-butene) $\leq 8 \cdot 10^{-17}$ cm³/s; k_7 (benzene) $\leq 3 \cdot 10^{-15}$ cm³/s; k_8 (toluene) $\leq 2 \cdot 10^{-14}$ cm³/s and k_9 (CCl₄) $\leq 1 \cdot 10^{-15}$ cm³/s. These limits did not change significantly even around 400 K.

Introduction

The interest in the reactivity of the phenyl radicals stems on both fundamental and applied aspects.

Phenyl represents the smallest of the aromatic (aryl) radicals. The free electron is in a sp²-orbital; the aromatic π -electron system is to a first approximation identical with that of benzene [1]. Therefore we may expect its reactivity to resemble that of other radicals with comparable electron configuration, i.e. vinyl, although modifications arising from entropy and energy differences should be anticipated. Moreover, by way of study of phenyl reactions it should be possible to characterize potential differences of this class of reagents compared to the well studied group of alkyl radicals.

The applied aspect concerning the reactivity of phenyl relates to its suggested participation in the formation mechanisms of polycyclic aromatic hydrocarbons (PAHs) and of soot [2, 3]. Detailed modelling of PAH and soot formation in flames has so far been impossible due to a lack of rates, mechanisms and thermochemistry of a large bulk of individual reactions that may be expected to be important. However, current knowledge suggests that PAH formation has to be subdivided into two major steps [2, 3]:

- formation of phenyl by the poly-condensation of C₂-species (C₂H₃, C₂H, C₂H₂)
- polymeric growth of phenyl in reactions with C_2H_3 , C_2H_2 or benzene.

Although PAH's must be considered trace components in most combustion systems which appear in fractional yields of only $10^{-6}-10^{-7}$ of the fuel [4], they are of considerable concern from the viewpoint of potential adverse health effects [5]. Therefore the oxidative prevention of PAH for-

mation such as by the reaction of phenyl radicals with O_2 [6] are central elements of pollution control.

In the present paper we report the first application of a direct detection method of phenyl in the gas phase. It will be shown that by using the 488 nm laser line absorption in the $\tilde{X}^2A_1 - \tilde{A}^2B_1$ transition phenyl can be detected with sufficient sensitivity to enable kinetic investigations of its reactions. To our knowledge this has not been achieved before. We consider the present work in which we have studied the reactions of phenyl with NO, NO₂ and O₂ and selected organics as a baseline case study on which further investigations at higher temperatures can be based. The present knowledge of the reactivity of phenyl is limited to liquid phase studies at low temperatures [7] and to indirect measurements in the flame temperature region [8.9].

Experimental

The present experiments have been performed using a combined laser photolysis/laser absorption technique. The experimental setup is shown schematically in Fig. 1. Briefly, it consists of a thermostated Duran glass reactor (100 cm length, 5.2 cm diameter) through which the gas mixture is slowly flown ($v \leq 20$ cm/s) in order to prevent accumulation of reaction products. The ends of the reactor are closed-off with spectrosil quartz windows of high geometrical quality ($\lambda/10$). Phenyl radicals are generated by the 248 nm excimer laser photolysis of substituted benzenes C₆H₅X (X = Cl, Br and NO). The configuration of the photolysis is coaxial. With precursor concentrations in the order of $5 \cdot 10^{14}$ cm⁻³ and a laser photon density of $\sim 2 \cdot 10^{16}$ cm⁻² the initial phenyl concentrations were typically $4 \cdot 10^{12}$ cm⁻³.

The detection of phenyl is performed by long path cw-laser absorption at 488 nm using an Ar^+ laser (COHERENT, CR 15) as a light source. The output of this laser is multiply folded across the reaction cell by means of two dielectrically coated mirrors in White configuration. Typical absorption path lengths with this set-up were

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Fig. 1

Schematic representation of laser photolysis/cw-laser absorption experiment

40 m. It should be noted that a set-up as shown in Fig. 1, with the White cell mirrors outside of the reactor, proofed to be essential for studies over a larger temperature range. Although with the White cell mirrors inside the reactor still larger path lengths (up to 100 m) can be achieved [10] the optics of this arrangement is thermally too instable to prevent measurements over an extended temperature range.

The transmitted laser beam is monitored with a fast photodiode (Hamamatsu S 1337-33) and then differentially amplified using a fraction of the unattenuated laser beam as a reference. The signal is stored in a digital oscilloscope and then averaged and analyzed by means of a microcomputer. With the averaging performed over 60 individual experiments, absorptions as low as 0.1%, corresponding to a phenyl concentration of $\sim 10^{11}$ cm⁻³ can be detected. All experiments were made in N₂ at total pressure of 50 ± 2 mbar.

Results and Discussion

i) The Absorption of Phenyl at 488 nm

Following the 248 nm excimer laser photolysis of precursor molecules such as chloro-, bromo- or nitrosobenzene we observe a transient absorptions of the 488 nm Ar^+ laser line. A representative example is shown in Fig. 2. Due to the approximate invariance of the observed absorption on the nature of the precursor we assigne this absorption to the only common fragment, phenyl.

A visible absorption of the phenyl radical in the wavelength region 430-530 nm has first been reported by Porter and Ward [1]. With the assignment of the ground state electronic configuration of phenyl of π^6 n the observed transition was interpreted as $\tilde{X}^2A_1 \tilde{A}^2B_1$ resulting from a π -n excitation. The observed spectrum revealed a series of vibrational bands with two fundamental frequencies at 571 and 896 cm⁻¹ which correspond to the e_{2g} and a_{1g} frequencies of the excited B_{2u} state of benzene. Fig. 3 is as synthesis spectrum constructed from the line positions and relative line intensities of Ref. [1]. As can be seen none of the vibrational line centers coincides with the Ar⁺-laser line. We therefore assume that the absorptions observed at 488 nm are due to the rotational structure of the vibrational band and, most likely, line broadening. If we assume the width of the vibration-rotation bands of phenyl to be roughly equal to those of the 260 nm band of benzene [11] the approximate synthesis spectrum of Fig. 3 is obtained which clearly shows absorption at 488 nm.



Transient absorption at 488 nm observed in the 248 nm excimer laser photolysis of C_6H_5X (X = Cl, Br and NO). The signal is the average over 60 individual laser pulses

The absorption cross section of phenyl at 488 nm has been determined from the observed initial absorption following the 248 nm photolysis of chloro- and bromobenzene. The corresponding phenyl concentration in these experiments is calculated from the relation

 $[Ph] = N_{p} \cdot [PhX] \sigma_{PhX}^{248} \cdot \varphi .$

Where [PhX] and σ_{PhX}^{248} are the phenyl precursor concentrations and cross sections (σ^{248} (chlorobenzene) = $3.0 \cdot 10^{-19}$ cm², σ^{248} (bromobenzene) = $3.9 \cdot 10^{-19}$ cm² [12]), respectively, and N_p is the number density of laser photons (typically $2 \cdot 10^{16}$ cm⁻²) as determined from laser pulse energy



Fig. 3

Synthesis spectrum of the visible $\tilde{X}^2A_1 - \tilde{A}^2B_1$ absorption band of phenyl as constructed from the line positions and relative line strengths of Ref. [1]. The arrow indicates the position of the 488 nm laser line

measurements. The quantum yield (φ) has been assumed to be unity. With both precursor molecules slightly different results for $\sigma_{Ph}^{488} = \ln (I_0/I)/[Ph] \cdot l$ are obtained: $\sigma_{Ph}^{488} = (6.4 \pm 3.3) 10^{-19} \text{ cm}^2$ from bromobenzene and $\sigma_{Ph}^{488} = (11.6 \pm 3.9) 10^{-19} \text{ cm}^2$ from chlorobenzene. We attribute this difference to a systematic error in the concentration, quantum yield and/or absorption coefficient of one of the precursors. Since the source of this error could not be identified unequivocally we recommend the mean value of the two, i.e.

$$\sigma_{\rm Ph}^{488} = (9 \pm 4) \, 10^{-19} \, {\rm cm}^2$$

as the best working value of the phenyl absorption cross section at 488 nm. Since this is the first determination of an absolute absorption cross section for phenyl in the visible region comparable literature values are not available.

It should be noted that a near UV contineous absorption of phenyl between 230-270 nm has previously been detected both in the condensed liquid [13, 14] and, more recently, in the gaseous phase [15]. Although the cross section in this UV band is likely to be larger than the average of the visible cross section, we have not attempted detection of phenyl in this wavelength region because it overlaps with that of the precursor molecules and many of the potential reagents. It is the advantage of the visible band of phenyl that it is essentially unique in the hydrocarbon system and therefore detection of phenyl in this band allows the unperturbed study of the kinetics of its reactions with a large number of molecules.

ii) Kinetics of Phenyl Reactions

With typical precursor concentrations of $(4-5) 10^{14}$ cm⁻³ the initial concentration of phenyl is generally in the order of $\sim 4 \cdot 10^{12}$ cm⁻³; the corresponding absorptions amount to $\sim 2\%$. In the absence of additional reagent the decay of phenyl occurs on a time scale of several 10 ms (cf. Fig. 2) and probably corresponds to a joint effect of reaction (with impurities in the precursor and with itself) and transport with a total first-order rate coefficient k'. It should be noted that the initial phenyl concentration could not be increased sufficiently to isolate the self-reaction phenyl + phenyl \rightarrow products. However, upon addition of reagents such as NO or NO₂ an acceleration of the phenyl decay could clearly be observed. A typical example of such decay traces is shown in Fig. 4 together with the logarithmic representation. As can be seen the decay is exponential; the pseudo-first order rate coefficient, $k_{1st} = \Delta \ln [Ph]/\Delta t = k$ $[NO_x] + k'$, is, apart from the constant k', proportional to the reagent concentration $[NO_x]$. In this and in all other experiments the total pressure was (50 ± 2) mbar of N₂.



Observed experimental absorption trace of phenyl in the presence of NO₂ and its logarithmic representation. [NO₂] = $3.25 \cdot 10^{13}$ cm⁻³, [Phenyl]₀ $\simeq 5 \cdot 10^{12}$ cm⁻³, T = 298 K, p = 50 mbar N₂



Fig. 5 Dependence of the first-order rate coefficient for (1) phenyl + NO \rightarrow products on the NO concentration; T = 297 K; p = 50 mbar N₂

1. Phenyl + NO \rightarrow Products

The resulting first order decay constants k_{1st} as a function of added NO for experiments at 297 K are shown in Fig. 5.

As can be seen there is a very satisfactory linear dependence from which we obtain for the rate coefficient $k_1 = (10.8 \pm 1.9) \ 10^{-12} \text{ cm}^3/\text{s}$. Together with an independent set of experiments performed at 298 K and for which $k_1 = (8.7 \pm 0.8) \ 10^{-12} \text{ cm}^3/\text{s}$ we obtain as the best room temperature value

 $k_1 (298 \text{ K}) = (9.5 \pm 1.5) \ 10^{-12} \text{ cm}^3/\text{s}.$

Similar experiments have also been performed at 351, 391 and 404 K. The resulting rate coefficients are summarized in Table I and represented in Arrhenius form in Fig. 6. As can be seen, the rate coefficients are slightly decreasing with increasing temperature. The corresponding Arrhenius experession is

$$k_1(T) = (4.0 \pm \frac{3.8}{1.9}) 10^{-12} \exp [300 \pm 100)/T] \text{ cm}^3/\text{s}$$

reflecting a negative activation energy of $E_A = -(2.4 \pm 1.8) \text{ kJ/mol.}$

Table 1 Summary of rate coefficients of phenyl reactions as determined in this work. All data refer to pressures of (50 \pm 2) mbar of N₂

Reagent	Т	$k/\mathrm{cm}^3\cdot\mathrm{s}^{-1}$
NO	297 298 351 391 404	$\begin{array}{c} (10.8 \pm 1.9) \ 10^{-12} \\ (8.7 \pm 0.8) \ 10^{-12} \\ (8.3 \pm 2.0) \ 10^{-12} \\ (7.9 \pm 1.5) \ 10^{-12} \\ (7.3 \pm 0.5) \ 10^{-12} \end{array}$
NO ₂	298 298 347 399	$\begin{array}{r} (8.2 \ \pm \ 1.1) \ 10^{-12} \\ (6.9 \ \pm \ 1.6) \ 10^{-12} \\ (6.7 \ \pm \ 1.6) \ 10^{-12} \\ (4.6 \ \pm \ 0.5) \ 10^{-12} \end{array}$
O ₂	298 407	$\leq 2 \cdot 10^{-17}$ $\leq 2 \cdot 10^{-17}$
C_2H_4	297 404	$\leq 8 \cdot 10^{-17}$ $\leq 6 \cdot 10^{-17}$
C_2H_2	297 489	$\leq 8 \cdot 10^{-16}$ $\leq 1 \cdot 10^{-15}$
2-butene	297 404	$\leq 8 \cdot 10^{-17}$ $\leq 9 \cdot 10^{-17}$
benzene	297 404	$\leq 3 \cdot 10^{-15}$ $\leq 3 \cdot 10^{-15}$
toluene	298 429	$\leq 2 \cdot 10^{-14}$ $\leq 8 \cdot 10^{-15}$
ССЦ	298 429	$\leq 1 \cdot 10^{-15}$ $\leq 3 \cdot 10^{-15}$

The absolute value of the rate coefficient and its slight negative temperature dependence may be taken as indirect evidence that this reaction occurs as a barrier free recombination forming nitrosobenzene, viz.

$$\bigcirc^{\bullet} + NO \longrightarrow \bigcirc^{-NO}$$
; $\Delta H_{R} = -218 \text{ kJ/mol}$ (1)

With the enthalpies of formation of ΔH_t (C₆H₅) = 328 kJ/ mol [16] and ΔH_t (C₆H₅NO) = 201 kJ/mol [17] this reaction is exothermic by 218 kJ/mol. No other reaction pathway seems thermodynamically feasible. Direct support of this conclusion comes from the experiments of Ikeda et al. [15], who in absorption experiments around 270 nm have directly observed the formation of nitrosobenzene.



Arrhenius representation of the rate coefficient for (1) phenyl + $NO \rightarrow products$

The rate coefficient k_1 at room temperature ($k_1 = (9.5 \pm 1.5) 10^{-12} \text{ cm}^3/\text{s}$) is almost identical to that of the reactions of other radicals of similar complexity (i.e. benzyl, o-methylbenzyl, p-methylbenzyl) with NO [18]. Moreover, even the rate coefficient for CH₃ + NO, which in the high pressure limit has been determined as $1.7 \cdot 10^{-11} \text{ cm}^3/\text{s}$ [19], is less than a factor of two different. This similarity may be taken as evidence that in this reaction phenyl behaves very much like a π/σ -radical with a reactivity resembling that of alkyl radicals despite the different hybridization. The character of phenyl as a π/σ -radical has been noted previously [20-22].

2. Phenyl + $NO_2 \rightarrow Products$

First order rate for the decay of phenyl in the presence of NO₂ for experiments at 298 K are shown in Fig. 7. The data presented correspond to a second order rate coefficient of $k_2 = (8.2 \pm 1.1) 10^{-12} \text{ cm}^3/\text{s}$. Together with the result from a second set of experiments performed at this temperature $(k_2 = 6.9 \pm 1.2) 10^{-12} \text{ cm}^3/\text{s}$) we obtain

$$k_2 (298 \text{ K}) = (7.5 \pm 1.2) \ 10^{-12} \text{ cm}^3/\text{s}$$

as our best room temperature value.

The results from additional experiments performed at 347 and 399 K are summarized in Table I and presented in Arrhenius from in Fig. 8. The corresponding Arrhenius expression devived from this figure is

$$k_{2}(T) = (1.3 \pm \frac{2.7}{0.8}) \, 10^{-12} \exp \left[(540 \pm 180)/T \right] \, \text{cm}^{3}/\text{s}$$

As for k_1 the rate coefficient k_2 is decreasing with increasing temperature, reflecting a negative activation energy of $E_A = -(4.5 \pm 2.8)$ kJ/mol).

Although there is a slightly stronger temperature dependence for the reaction with NO₂, the error limits in E_A and in the absolute rate coefficients virtually overlap with those for phenyl + NO. However, compared to reaction (1) the



Fig. 7 Dependence of the first-order rate coefficient for (2) phenyl + NO₂ \rightarrow products on the NO₂ concentration, T = 298 K, p = 50 mbar N₂



Fig. 8 Arrhenius representation of the rate coefficient for (2) phenyl + $NO_2 \rightarrow products$

reaction between phenyl and NO_2 has several exothermic product routes, viz.

$$\bigcirc^{\bullet} + NO_{2} \longrightarrow \bigcirc^{\bullet} NO_{2} \qquad \Delta H_{R} = -293 \text{ kJ/mol}$$

$$\longrightarrow \bigcirc^{\bullet} ONO \qquad \Delta H_{R} = \sim -283 \text{ kJ/mol}$$

$$\longrightarrow \bigcirc^{\bullet} O^{\bullet} + NO \quad \Delta H_{R} = -(222 \pm 8) \text{ kJ/mol}$$
(2)

With the enthalpies of formation taken as ΔH_f (nitrobenzene) = 87 kJ/mol [23, 24], ΔH_f (phenylnitrite) ~97 kJ/mol [24] and ΔH_f (phenoxi) = 48 ± 8 kJ/mol [23] these reaction pathways are exothermic by 293, ~283 and 222 ± 8 kJ/ mol, respectively. We have no possibility to differentiate between either of these product routes. The nature of the overall rate coefficient, however, suggests that the kinetics is governed by a barrierless recombination with an interaction potential similar as in the reaction of phenyl with NO. That one of the primary recombination products such as excited phenyl-ONO may decompose the yield phenoxi + NO is highly likely but the occurence of this bimolecular reaction channel is apparently not reflected in the nature of the overall kinetics. It should be noted that the reaction between CH₃ + NO₂ for which the rate coefficient ar room temperature has been determined as $k = 2.5 \cdot 10^{-11}$ cm³/s [25] proceeds entirely by the O-atom metathesis mechanism yielding CH₃O + NO [25].

The rate coefficient between phenyl and NO₂ has to our knowledge not been determined before. However, Tsang et al. [26] have recently studied the thermal decomposition of nitrosobenzene in a shock tube experiment between 1070-1180 K. From the observed products (phenyl + NO₂) and with the conversion of their measured dissociation rate coefficients into the reverse association a rate coefficient of (0.7-2.0) 10^{-12} cm³/s has been derived for the recombination between phenyl and NO₂ at this temperature. This is in very satisfactory agreement with the value for k_2 as obtained by extrapolation of our measurements (k_2 (1100 K) $\simeq 2 \cdot 10^{-12}$ cm³/s).

3. Phenyl + $O_2 \rightarrow$ Products

The reaction between phenyl and O_2 has been studied at 298 and 407 K by observing the temporal behaviour of the 488 nm absorption following the 248 nm photolysis of nitrosobenzene in the presence of O_2 . However, even with 50 mbar of O_2 no significant acceleration of the decay of transient absorption could be observed. Assuming that a change of the decay constant of 20 s⁻¹ is measurable, this result transfers into an upper limit of the rate coefficient k_3 of

$$k_3$$
 (298 and 407 K) $\leq 2 \cdot 10^{-17}$ cm³/s

The apparent low reactivity between phenyl and O_2 is surprising since one would expect that this reaction occurs readily forming a peroxi radical, viz.

$$\bigcirc^{\bullet} + \circ_2 \longrightarrow \bigcirc^{-\circ\circ^{\bullet}}$$
(3)

For smaller alkyl radicals, for instance, this reaction type occurs with a rate coefficient between $(2.2-15) \ 10^{-12} \ cm^3/s$ [27] in the high pressure limit; the alkylperoxi radicals being thermally stable (BDE (R-O₂) > 100 kJ/mol) at room temperature. The following possibilites are suggested to explain the "unobserved" reaction between phenyl and O₂:

Firstly, the reaction could be kinetically inhibited through the existence of an activation barrier to recombination. Although this is in contrast to the observations made for alkyl $+ O_2$, it must be noted that, compared to alkyl, the free election in phenyl is in a differently hybridized orbital (sp² vs. sp³). As a consequence there may be a repulsive interaction between the π -system of phenyl with the p-orbitals of O_2 . We are not aware of any quantum chemical calculation, however, where this has been predicted.

Secondly, the reaction between phenyl and O_2 could be rapidly equilibrating with no substantial loss of phenyl. Assuming a detectable loss of phenyl of ~10% of its initial concentration (~4 \cdot 10¹² cm⁻³) upon equilibration with phenyl-O₂, then with $[O_2] = 1.2 \cdot 10^{18} \text{ cm}^{-3}$ the required equilibrium constant, $K_3 = [PhO_2]/[Ph] [O_2]$, is estimated as $\leq 1 \cdot 10^{-19} \text{ cm}^{-3}$, which at 300 K transfers into $K_p \leq$ 2.4 atm⁻¹ and $\Delta G_R > -2.17 \text{ kJ/mol}$. Together with a sensible assumption for the entropy change for reaction (3) ($\Delta S_R \simeq -120 \text{ J/mol} \cdot \text{K}$) the corresponding bond strength for phenyl-O₂ would be predicted as $\Delta H_R \leq 42 \text{ kJ/mol}$. This is less than half the value for alkyl-O₂ and hence unusually low for peroxi radicals. A larger bond strength would only be consistent with our observation in conjunction with a barrier to recombination.

Thirdly, an "unobserved" reaction between phenyl and O_2 could also be the result of an experimental artifact via the interference of the 488 nm absorption of phenyl by the product phenyl- O_2 . Peroxi radicals such als HO₂ and alkyl- O_2 have strong near UV absorptions. At least for HO₂ an additional weak electronic transition near 1.25 µm is also known [28]. Whether any of these is sufficiently shifted for phenyl- O_2 to create a visible absorption near 488 nm is presently unknown. In any case it would be difficult to envisage comparable absorptivities of phenyl and phenyl- O_2 which would be essential to explain our observations.

We are presently unable to differentiate between these there possibilities. Clearly, absorption experiments at different wavelength would help to resolve the problem of overlapping absorptions. The question of activation barriers and/or insufficient phenyl-O₂ stability can only be resolved in experiments over a still larger temperature range, including T < 300 K. It should be noted, however, that the present findings do not exclude the possibility of a high temperature bimolecular reaction.

$$O^{\bullet} + O_2 \longrightarrow O^{\bullet} + O^{\bullet} \Delta H_{R} = -31 \text{ kJ/mol}$$

which has been suggested by Euchner et al. [6].

4. Reactions with Selected Organics

The reactions of phenyl radicals with selected organics $(C_2H_4, C_2H_2, 2$ -butene, benzene, toluene and CCl₄) have been studied using chlorobenzene or nitrosobenzene as a source of phenyl at total pressures of 50 mbar of N₂. Each compound was investigated at two different temperatures. However, even at the highest temperature employed no systematic acceleration of the phenyl decay in the presence of the organic was noted. As a consequence we can only derive upper limits for any of the rate coefficients. The data are summarized in Table I.

To our knowledge there has been only one single previous study of the rate coefficient for phenyl with benzene, toluene and CCl₄ by Scaiano and Stewart [7]. These authors found k (benzene) = $7.5 \cdot 10^{-16}$ cm³/s, k (toluene) = $2.8 \cdot 10^{-15}$ cm³/s and k (CCl₄) = $1.3 \cdot 10^{-14}$ cm³/s. Although the experiments of [7] were performed in the condensed liquid phase they still allow some comparision with our results (cf. Table I and Fig. 9). Whereas for benzene and toluene our upper limits are consistent with the data of Scaiano and Stewart, our limit for CCl₄ is an order of magnitude lower than that of [7]. We have presently no explanation for this disparity.



Fig. 9

Arrhenius representation of the rate coefficients for the reactions of phenyl with benzene, toluene, C₂H₄, C₂H₂, 2-butene and CCl₄. FMS: Fahr et al. [9]. Open symbols: Scaiano and Stewart [7]; filled symbols: this work (upper limits only)

The only other gas phase study of reactions of phenyl with organics (C₂H₄, C₂H₂ and benzene) has been performed by Fahr et al. [9]. These authors determined the rate coefficients for these reactions around 1030 K by a relative technique using the recombination of phenyl with a rate coefficient of $5 \cdot 10^{-12}$ cm³/s as a reference. They obtained k $(C_2H_4) = 2.0 \cdot 10^{-13} \text{ cm}^3/\text{s}, k (C_2H_2) = 2.7 \cdot 10^{-13} \text{ cm}^3/\text{s} \text{ and}$ k (benzene) = $4.9 \cdot 10^{-14}$ cm³/s, i.e. a considerably higher rate for C_2H_4 and C_2H_2 compared to benzene. Moreover, by assuming a pre-exponential factor of $5.25 \cdot 10^{-13}$ cm³/s (identical for all three reactions) Fahr et al. also derived Arrhenius expressions, a graphical representation of which is shown in Fig. 9. Although the physical significance of extrapolation of these expressions to room temperature is rather limited we find a consistency with our data for the case of benzene only. For C_2H_2 and C_2H_4 , on the other hand, our upper limits are substantially lower (by several orders of magnitude) than those predicted by extrapolation of the Fahr et al. data. Since it is difficult to envisage that an Arrhenius graph has negative curvature, i.e. activation energy decreasing with increasing temperature, we conclude that the temperature dependence of k (C_2H_4) and k (C_2H_2) as derived by Fahr et al. is probably too weak.

The reactions of phenyl radicals with hydrocarbons can in principle proceed by two distinct different routes: abstraction of an H-atom or addition to a π -system. From the C-H bond strength in benzene (464 kJ/mol, corresponding to $\Delta H_{\rm f}$ (phenyl) = 329 kJ/mol [29]) it follows that phenyl may undergo exothermic abstraction reactions with all alkanes and that these exothermicities will even be larger that those for reactions of CH₃ radicals (BDE (CH₃-H) = 439 kJ/mol [16, 29]). Unfortunately, there are no data available for such comparision. For reactions of phenyl with unsaturated and aromatic hydrocarbons the abstraction routes are thermoneutral (C_2H_4 , benzene) or endothermic (C_2H_2) and therefore we expect the addition process to be the only active interaction pathway. Comparable reactions of CH₃ have been studied [30]. Upon extrapolation to 300 K rate coefficients in the order of $2 \cdot 10^{-18}$ cm³/s for C₂H₄, C₂H₂ and benzene as reagents are obtained. These data are still lower than the upper limits of the corresponding rate coefficients for phenyl reactions as obtained in this work. As a consequence we conclude that our upper limits may be well above the true rate coefficients and that reaction between phenyl and these compounds may only be observed at substantially higher temperatures.

The reaction of phenyl with CCl₄ my energetically occur as a simple Cl-atom metathesis reaction forming chlorobenzene + CCl₃ ($\Delta H_R = -94$ kJ/mol [29]). The low rate coefficient observed despite this exothermicity, however, is entirely consistent with the picture of phenyl as a low reactivity radical.

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Absolute Raman Intensities of the Carbonyl Stretching Band in Para Substituted Methyl Benzoates

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Spectroscopy, Raman / Spectroscopy, Ultraviolet

The absolute Raman intensities of the $v_{C=0}$ band of para substituted methyl benzoates have been measured in CCl₄ solution at different excitation frequencies. The intensities depend on a preresonance Raman effect (PRRE) and are correlated with theoretical expressions which describe the dispersion of the Raman intensity as a function of the excitation frequency and the experimental UV frequencies of the compounds, in particular the $\pi \rightarrow \pi^* \, {}^1L_a$ band. – The Raman intensities free from PRRE are deduced by extrapolating the experimental values to a zero excitation frequency. These extrapolated intensities depend on the electron donating character of the substituents and on the extent of the conjugated system. – The depolarization ratio of the $v_{C=0}$ band in methyl benzoates increases with the excitation character of the substituted derivatives.

Introduction

In previous works we have been concerned with the influence of hydrogen bonding on the Raman intensity of the $v_{C=0}$ band in aliphatic esters [1,2] and ketones [3,4]. It was shown that the intensity increased on hydrogen bonding. From other literature data it is clear that the Raman intensity is very sensitive to conjugation effects [5-13]. To have a better understanding on the effect of conjugation on the Raman intensity of the $v_{C=O}$ band, the effect of para substitution on the Raman intensity of the $v_{C=O}$ band in

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