
TRANSPORT PHENOMENA *in* COMBUSTION

• V O L U M E 1 •

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TRANSPORT PHENOMENA IN COMBUSTION, Volumes 1 & 2

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RATE COEFFICIENTS FOR THE FAST REACTIONS OF PHENYL RADICALS WITH NO AND O₂ FROM MASS SPECTROMETRIC MEASUREMENTS OF PHENYL DECAYS.

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ABSTRACT

The multichannel reactions $\Phi + O_2$ and $\Phi + NO$ ($\Phi = C_6H_5$) have both been studied in a fast flow reactor in the temperature range 418 to 815 K and at a pressure of 0.7 mbar. Phenyl radicals were produced by the pyrolysis of nitrosobenzene, ΦNO . For the first time kinetic results have been obtained for these reactions through mass spectrometric measurements of phenyl decays in a large excess of O_2 and NO , respectively. Below 500 K the measured rate coefficient for $\Phi + NO$ (reaction 1) is in good agreement with the recent results of Yu and Lin /1/ for this reaction. At higher temperatures the reaction shows fall off behavior which has not been previously observed. For $\Phi + O_2$ (reaction 2) we obtain between 418 - 815 K and 0.7 mbar the total rate expression $k_{2tot} = 3.8 \times 10^{-11} \exp(-290/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for this multichannel reaction. This result is several orders of magnitude higher than previous determinations of k_{2tot} by phenyl decays /cf. 2/. However, in the overlapping temperature regime it is in good agreement with a very recent study by Lin and coworkers /3/ in which the rate coefficient for collisional stabilization was determined from product measurements. This suggests that in the 300 - 800 K temperature range collision stabilization to ΦOO radicals is far more important than previously assumed. Calculations of k_{2tot} /3/ predict a minimum around 700 - 800 K which has not been observed in this work.

INTRODUCTION

The reactions of phenyl radicals play a key role in degradation mechanisms of aromatic compounds because side chains are almost always lost first so that phenyl or phenoxy radicals are formed which may finally undergo ring breaking reactions /5/. Another important issue is the potential relevance of phenyl reactions in soot formation. Here a competition arises between phenyl oxidation reactions and its association reactions with other hydrocarbons to form larger molecules /4/. For oxidation, the reaction $\Phi + O_2$

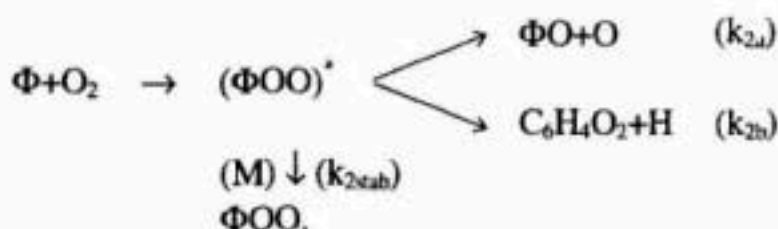
¹ Corresponding author

obviously plays a dominant role. Unfortunately, its rate coefficient is still uncertain and the literature data are spread over several orders of magnitude.

Preidel and Zellner /6/ have reported an upper limit for the $\Phi+O_2$ rate coefficient of 2×10^{-17} cm³/sec at around ambient temperatures. In a later study by this same laboratory /7/ k_{2to} was found to increase from 2.1×10^{-16} cm³/sec at 298 K to 1.7×10^{-14} cm³/sec at 905 K. Quite recently, Yu and Lin /2/ measured a value of 3.9×10^{-15} cm³/sec at 300 K. In all of these studies the rate coefficients were deduced from the temporal behavior of phenyl signals obtained through absorption measurements. Somewhat exceptional in this regard is the study by Walker and coworkers /8/. Here, a rate coefficient of $k_{2to} = 5.3 \times 10^{-13}$ cm³/sec was obtained at 773 K and 500 Torr pressure by adding benzene to slowly reacting H₂/O₂ mixtures.

These low numbers for k_{2to} have recently been questioned by Louw and coworkers /9/ who compared the rate of the gas phase $\Phi + O_2$ reaction with the rate of the liquid phase (H₂O) reaction.

An explanation for the small rate coefficients found in /2, 6 and 7/ has very recently been provided by another study of Lin and coworkers /3/ ². They found that phenyl absorption measurements were interfered with by the co-absorption of a reaction product of $\Phi+O_2$. Thus the rate coefficients deduced in /2, 6 and 7/ are too small. Lin and coworkers assumed that this product was collisionally stabilized ΦOO and from the measured rate of its appearance between 297 and 473 K they deduced a rate for the stabilization channel, k_{2stab} in the order of 1.5×10^{-11} cm³/sec. Thus the typical overall picture emerges for a reaction via a bound intermediate



Obviously, it would be desirable to measure the rate coefficient of the entrance channel, i.e. k_{2to} which means measuring phenyl profiles in an excess of O₂. An inversed stoichiometry is prohibited by the poorly known phenyl self-reaction for which only estimations of the rate coefficient exist /10/.

The above points raise the following questions:

- If phenyl decay curves are monitored by a method other than laser absorption would they yield a rate coefficient which is significantly larger than those in the earlier literature /2, 6 and 7/?
- Would this rate coefficient corroborate the data of Lin and coworkers /3/: These data were assumed to represent the stabilization channel and which, in this case, at low to moderate temperatures should be equal to those of the entrance channel?

² We gratefully acknowledge that Dr. Lin supplied us with a preprint.

Transport Phenomena in Combustion, Volume 1

- What happens at higher temperatures when the ΦOO radicals become less stable and where high temperature channels may eventually dominate?

Our detection method is electron impact mass spectrometry which required us to deal with nitrosobenzene fragments of the same mass as phenyl. In order to check our correction procedure we used the reaction $\Phi+\text{NO}$. Its rate coefficient, k_1 is of comparable size to that of $\Phi+\text{O}_2$ so that it can be measured under the same conditions. Moreover, k_1 is rather well known from the literature /1, 6/. In addition, since both reactions occur via similar bound intermediates, comparable fall off effects should be expected at the higher temperatures.

EXPERIMENTAL

Our flow reactor consists of a 25.5 mm i.d. quartz tube of 55 cm length which was either HF washed without any further coating or was teflon coated for some of the measurements below 500 K. The design of the heating block and its suspension were described in a recent paper /11/ as was the coupling to the mass spectrometer. Typical working pressures were around 0.7 mbar and the flow velocities ranged between 20 and 30 m/s. Under these conditions the usual corrections for flow effects /12/ are easily accounted for.

Only features which are specific to this study will be reported here. These include the pyrolytic radical source, wall loss of the radicals, and fragmentation in the mass spectrometer.

Phenyl Radical Source

For the production of alkyl radicals in a discharge flow reactor the reaction of F atoms with the respective alkane is a convenient radical source. By contrast, phenyl radicals cannot be produced in this way because $\text{F}+\text{C}_6\text{H}_6$ proceeds only to a minor extent via H abstraction, the main channel being F addition followed by H elimination /13/. We have found the same behavior for the reaction $\text{Cl}+\text{C}_6\text{H}_6$.

Photolysis of nitrosobenzene has been widely used in the literature /2, 3, 6/ in quasi-static experiments. Unfortunately it is not compatible with the flow reactor geometry. Stein and coworkers /10/ have described the use of nitrosobenzene as a pyrolytic source in their VLPP reactor.

We also used pyrolysis, but not in the form of a fixed source at the upstream end of the reactor because in this case the radicals would have been subjected to an enhanced wall loss between reactor walls and movable injector /14/. We chose to use a movable phenyl source and for this purpose a small tungsten coil (20mm length, 5mm diam., copper leads) was placed into the movable injector at a distance of about 2 cm from the exit holes. A heating power of about 40 W was needed to obtain temperatures around 1200 K at the coil. The performance of this pyrolytic source is shown in Fig. 1 as a function of the temperature. Under typical operating conditions we found approximately 80% dissociation of nitrosobenzene. An upper limit for the generated phenyl concentration is given by the absolutely measured NO yields. A fraction of the Φ radicals underwent subsequent reactions within the source to form benzene which

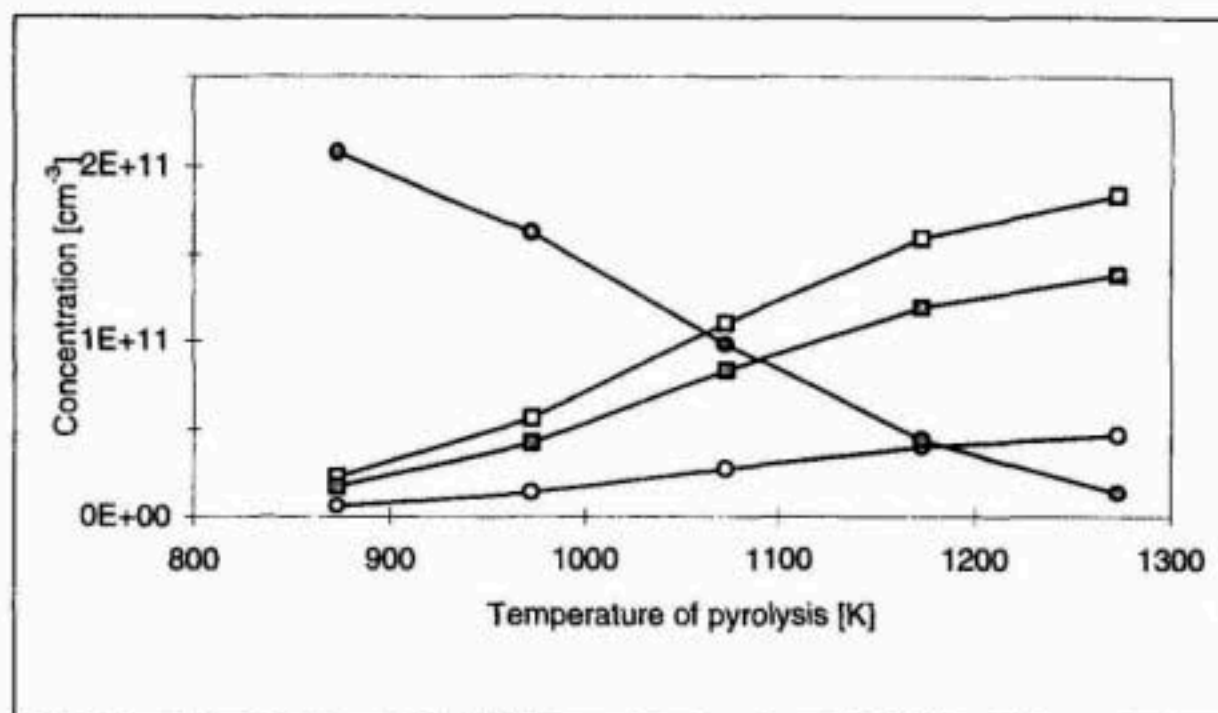


Figure 1. Performance of the phenyl source. Solid circles: Nitrosobenzene (conc. approx.). Open squares: NO (calibrated). Solid squares: Phenyl (conc. approx.). Open circles: Benzene (calibrated).

was also measured quantitatively. Since no other stable compounds were detected we used as an estimate $[\Phi]_0 = [\text{NO}] - [\text{C}_6\text{H}_6]$.

To avoid condensation problems, nitrosobenzene was allowed to vaporize from a heated reservoir directly into a large flow of He. With suitable temperature control the mixtures obtained turned out to be very stable, but were uncalibrated. Due to low vapor pressure of ΦNO the maximum achievable ΦNO flows were small. Hence at best $[\Phi]_0 = 1.5 \times 10^{11} \text{ cm}^{-3}$ was obtained at the exit holes of the source, the initial concentrations for the kinetic measurements being smaller. Finally, this phenyl source limited our reactor temperature to about 800 K because at considerably higher temperatures ΦNO would have partly decayed upstream of the pyrolytic oven.

The influence of the pyrolysis oven on the reactor temperature is small (see /11/).

Wall Loss of the Radicals

These effects may be very severe for aromatic radicals. For example, for ΦO radicals Hoyermann and coworkers /15/ have recently measured wall coefficients between 300 and 800 sec^{-1} at 300 K. This is roughly a factor of 100 more than one would normally expect in flow reactor work so that here a limitation of the method may arise.

Consequently, we paid particular attention to these effects by measuring phenyl signals upon displacement of the movable injector. The results are shown in Fig. 2. After preparation of a "new" reactor surface about 2 hours were needed to "run it in". Afterwards very constant and reproducible wall coefficients were obtained regardless of whether the reactor was used for $\Phi + \text{O}_2$ or $\Phi + \text{NO}$. A boronoxide coating gave virtually no improvement. Teflon coatings, however, gave a significant improvement but were only usable at temperatures below 500 K.

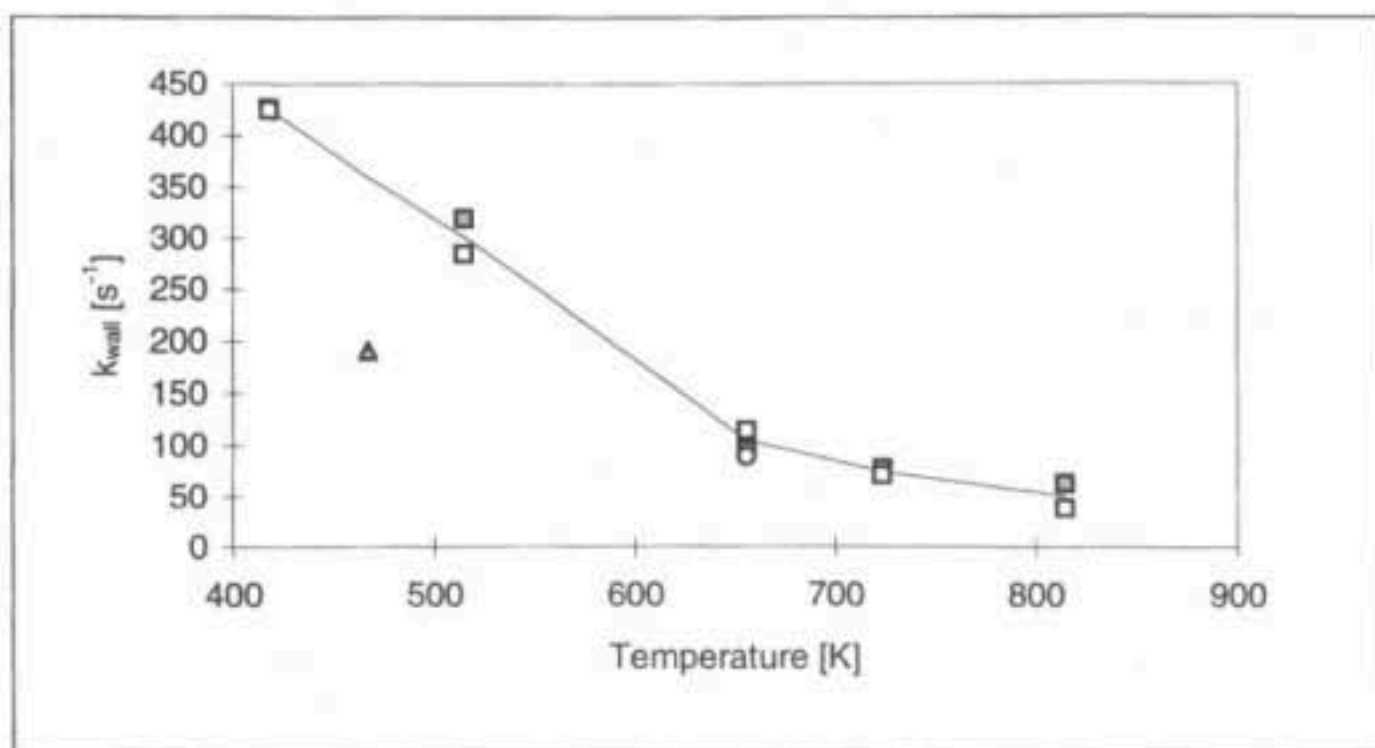


Figure 2. Temperature dependence of the wall loss coefficients. Solid squares: Quartz, HF washed (Φ +NO series). Open squares: Quartz, HF washed (Φ +O₂ series). Solid triangle: Teflon. Open circle: Boronoxide

The most remarkable effect of the walls is the decrease of the wall coefficient with increasing the temperature. This type of behavior is consistent with an adsorption-desorption mechanism. As a consequence, these flow reactor experiments are less influenced by the reactor walls at higher temperatures.

Mass Spectrometric Fragmentation

Under our conditions, the stable species emitted from our phenyl source which

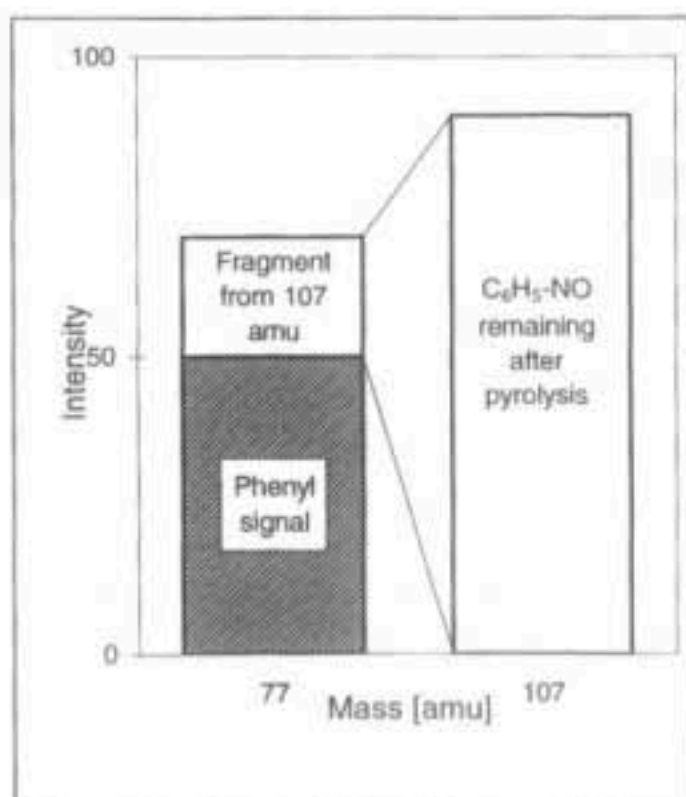


Figure 3a. Composition of the mass 77 signal consisting of phenyl and fragment of nitrosobenzene (parent mass 107).

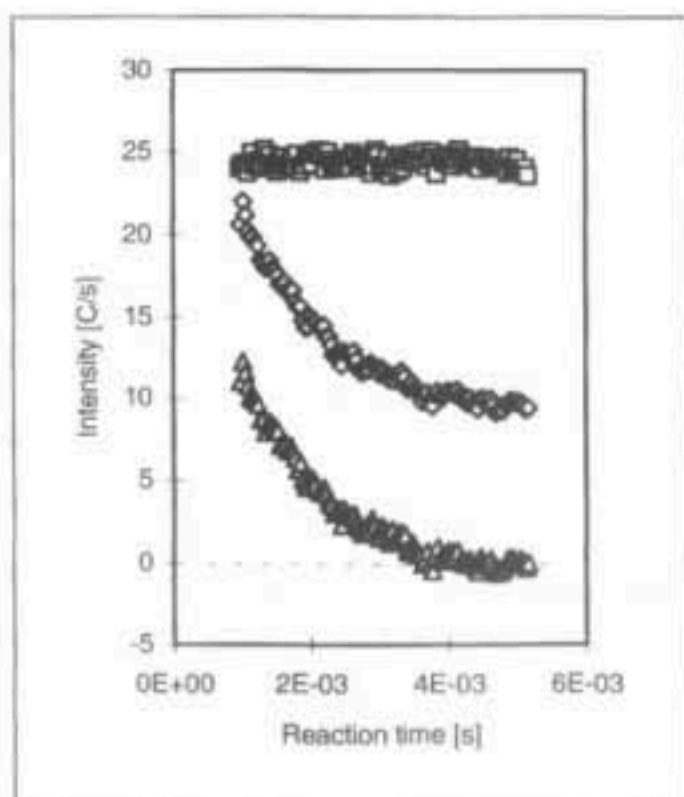


Figure 3b. Correction of a 77 amu profile (Φ +O₂). Squares: 107 amu. Diamonds: 77 amu. Triangles: corrected Phenyl signal.

may interfere with our phenyl signals through fragmentation are benzene and nitrosobenzene. The contribution of benzene may be avoided by using an electron energy below 13.5 eV. Consequently, we used generally 13.0 eV. Nitrosobenzene fragments cannot be minimized so easily because of the weak Φ -NO bond. As shown in Fig. 3, the contribution of Φ NO was corrected for by simultaneous measurements of 77 amu signals (phenyl+fragment) and 107 amu signals (nitrosobenzene). The contribution of the fragment which may be time dependent had to be subtracted. Its relationship to the nitrosobenzene signals was determined either by switching off the pyrolysis heater or by scavenging phenyl radicals in a very large excess of O_2 , both methods giving the same results. No other species that might interfere with the phenyl signals were found.

Purity of the gases and reagents used: He 5.0 (AGA Gasses); O_2 6.0 (AGA gasses); NO 4.0, 1% in He 5.0 (Air Liquide); C_6H_5NO 99% (Fluka chemicals).

RESULTS OF THE KINETIC EXPERIMENTS

Φ +NO

The usual pseudo-first order procedure was applied as demonstrated in Figs. 4 and 5. At a given temperature at least 7 and sometimes up to 15 independent phenyl profiles were measured for a given NO excess concentration. The concentration ranges of NO used along with the results are summarized in Tab. 1. It can be seen that the NO excess ranged from a minimum of 50 fold to nearly 1000 fold. The direction of the injector

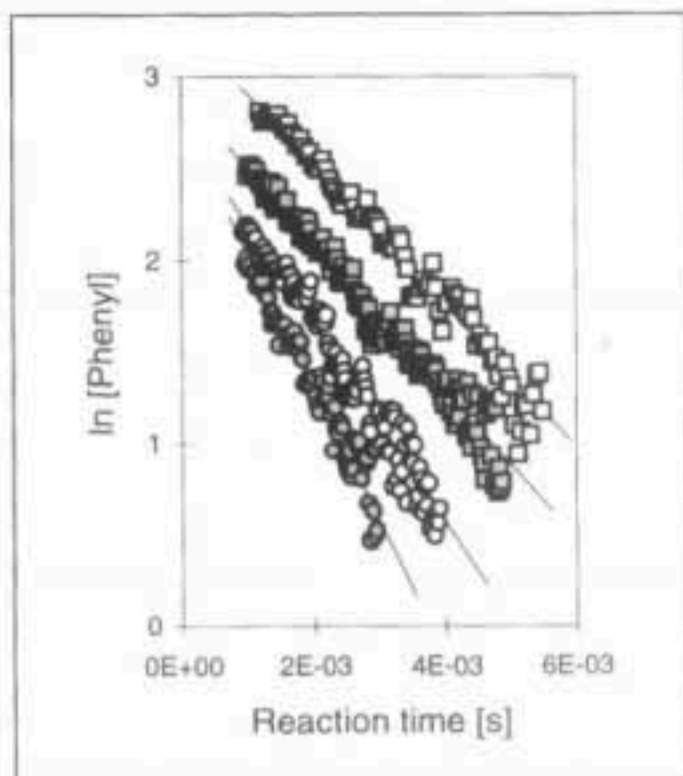


Figure 4. Phenyl decay curves for Φ +NO at 515 K. Concentrations of the excess component NO in cm^{-3} : 2.95×10^{12} (open squares), 8.86×10^{12} (solid squares), 1.77×10^{13} (open circles), 2.94×10^{13} (solid circles).

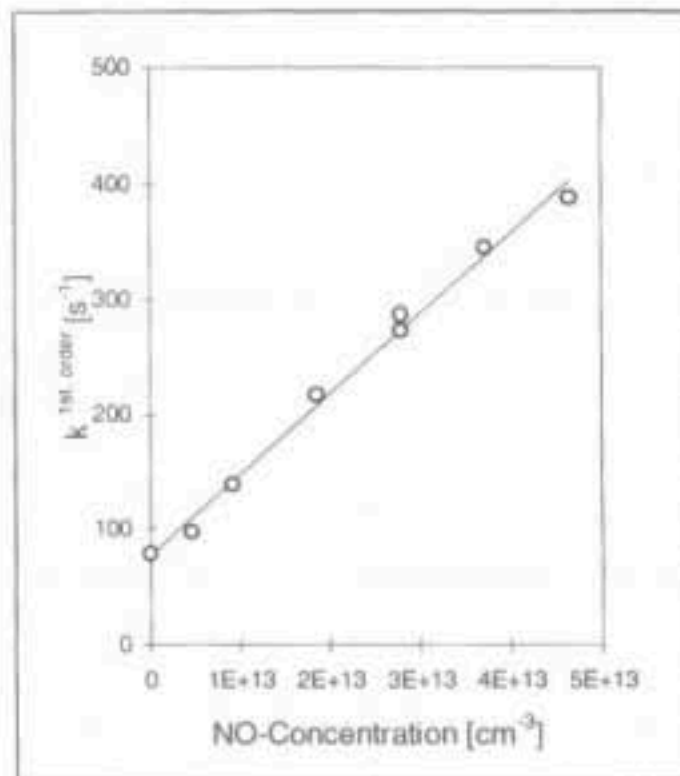


Figure 5. First-order plot for the reaction Φ +NO at 724 K.

Transport Phenomena in Combustion, Volume 1

Table 1. Experimental conditions and results for the Φ +NO series.

Temperature [K]	Pressure [mbar]	NO-Conc. [10^{13} cm^{-3}]	k_{0i} [$10^{12} \text{ cm}^3 \text{ s}^{-1}$]	k_{wall} [s^{-1}]
418	0.70	0-4.02	11.4	426
515	0.77	0-8.45	7.07	296
694	0.77	0-6.72	3.97	82
793	0.77	0-5.27	2.90	70
815	0.78	0-3.61	3.13	62
805	10.6	0-18.8	2.88	75

movement did not affect the profiles, i.e. we were not subjected to a change of wall conditions. Wall coefficients were not deduced from extrapolation but measured through individual phenyl profiles for $[\text{NO}]=0$. Typical phenyl decay curves are shown in Fig. 4 for 515 K. Phenyl concentrations were monitored over a change of only 1 order of magnitude. This was due to the relatively large scatter arising from our small initial concentrations and particularly from the automatic subtraction procedure which accounted for the fragmentation of nitrosobenzene. The nitrosobenzene was composed of Φ -NO which had survived the pyrolysis source and of Φ -NO formed by the reaction Φ +NO. The latter case giving the largest contribution. The profiles yielded first order rate coefficients. Their plot as a function of the excess concentration (Fig. 5 is an example at 724 K) shows that we have first-order kinetics with respect to NO. Fig. 5 also shows that it was always possible to make the gas-phase contribution large in comparison to the heterogeneous effects.

Our bimolecular rate coefficients are plotted in Arrhenius form in Fig. 6 along with the results of Yu and Lin /1/ and Preidel and Zellner /6/.

Our relatively large error bar refers to the estimation of the fragment on mass 77 amu. We also observe fall off effects which are discussed later. Below 500 K the measured rate coefficient for Φ +NO is in good agreement with the recent results of Yu

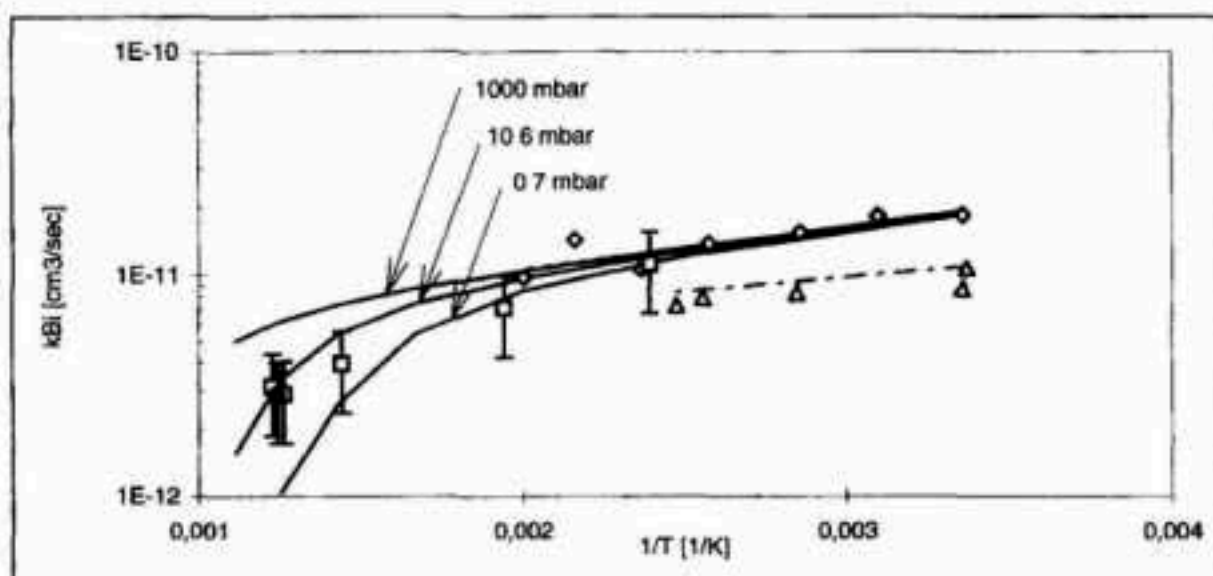


Figure 6. Arrhenius plot for the reaction Φ +NO. Open squares: this work at 0.7 mbar. Filled circle: this work at 10.6 mbar. Open diamonds: Yu and Lin /1/. Open triangles: Preidel and Zellner /6/. Solid lines are the result of Troe /17/ calculations

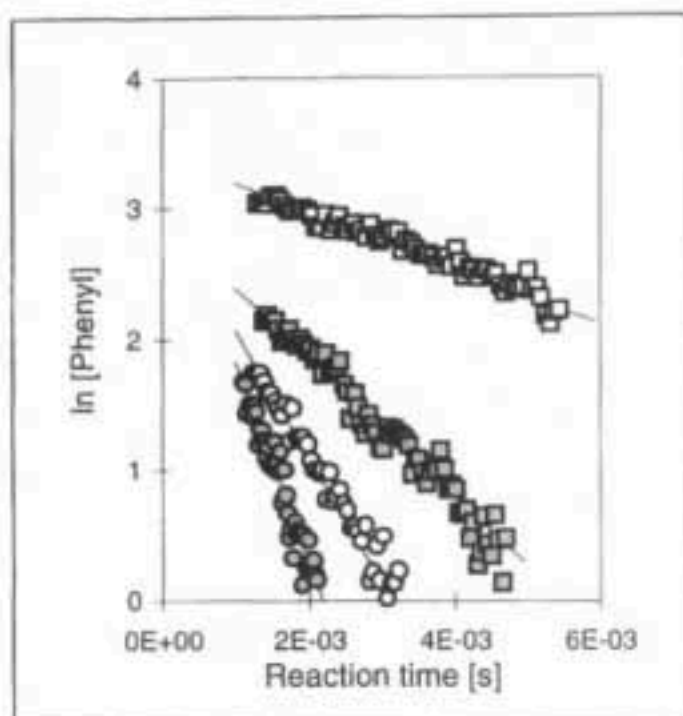


Figure 7. Phenyl decay curves for $\Phi + \text{O}_2$ at 515 K. Concentrations of the excess component O_2 in cm^{-3} : $\text{O}_2 = 0$ (open squares), 9.22×10^{12} (solid squares), 3.69×10^{13} (open circles), 1.84×10^{14} (solid circles).

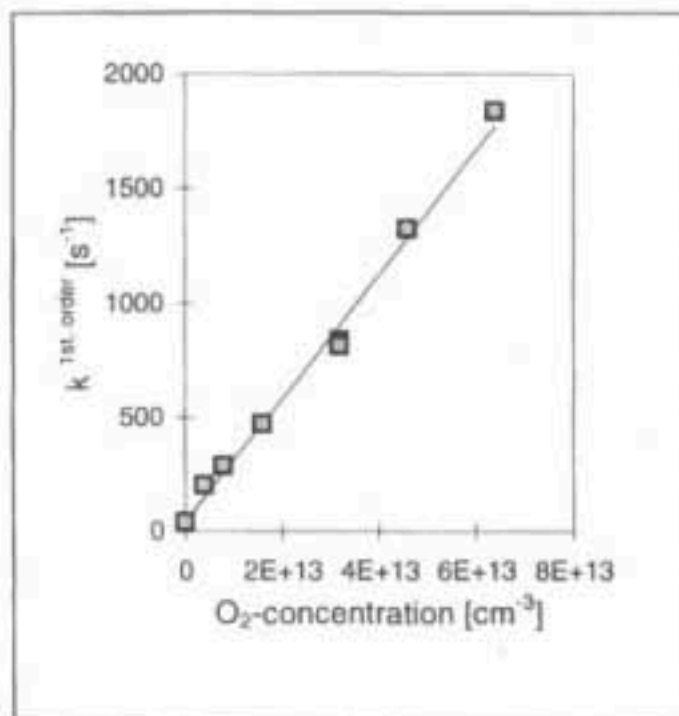


Figure 8. First-order plot for the reaction $\Phi + \text{O}_2$ at 815 K.

and Lin /1/ for this reaction (figure 6).

$\Phi + \text{O}_2$

We applied the same procedure as for $\Phi + \text{NO}$, however the $\Phi + \text{O}_2$ measurements were easier to perform because we could use O_2 as a pure gas so that larger concentrations could be introduced without affecting the total flow. In addition, nitrosobenzene is no longer a reaction product so that less fragments have to be accounted for. As a consequence, the scatter in the profiles is smaller. Fig. 7 shows phenyl decay profiles at 515 K. Fig. 8 is an example of the resulting first-order decay plots, the results of which are summarized in Table 2 along with the experimental conditions. An Arrhenius plot incorporating the literature data is shown in Fig. 9. Our results are several orders of magnitude higher than the earlier data, but again in the region of temperature overlap, there is good agreement with the very recent measurements of Yu and Lin /3/. Our

Table 2. Experimental conditions and results for the $\Phi + \text{O}_2$ series.

Temperature [K]	Pressure [mbar]	O_2 -Conc. [10^{13} cm^{-3}]	kBi [$10^{11} \text{ cm}^3 \text{ s}^{-1}$]	k_{wall} [s^{-1}]
418	0.70	0-4.02	1.97	424
515	0.63	0-18.4	1.94	285
656	0.30	0-1.52	2.83	114
724	0.70	0-10.9	2.27	70
793	0.77	0-6.26	2.59	48
815	0.77	0-6.39	2.70	38

Transport Phenomena in Combustion, Volume 1

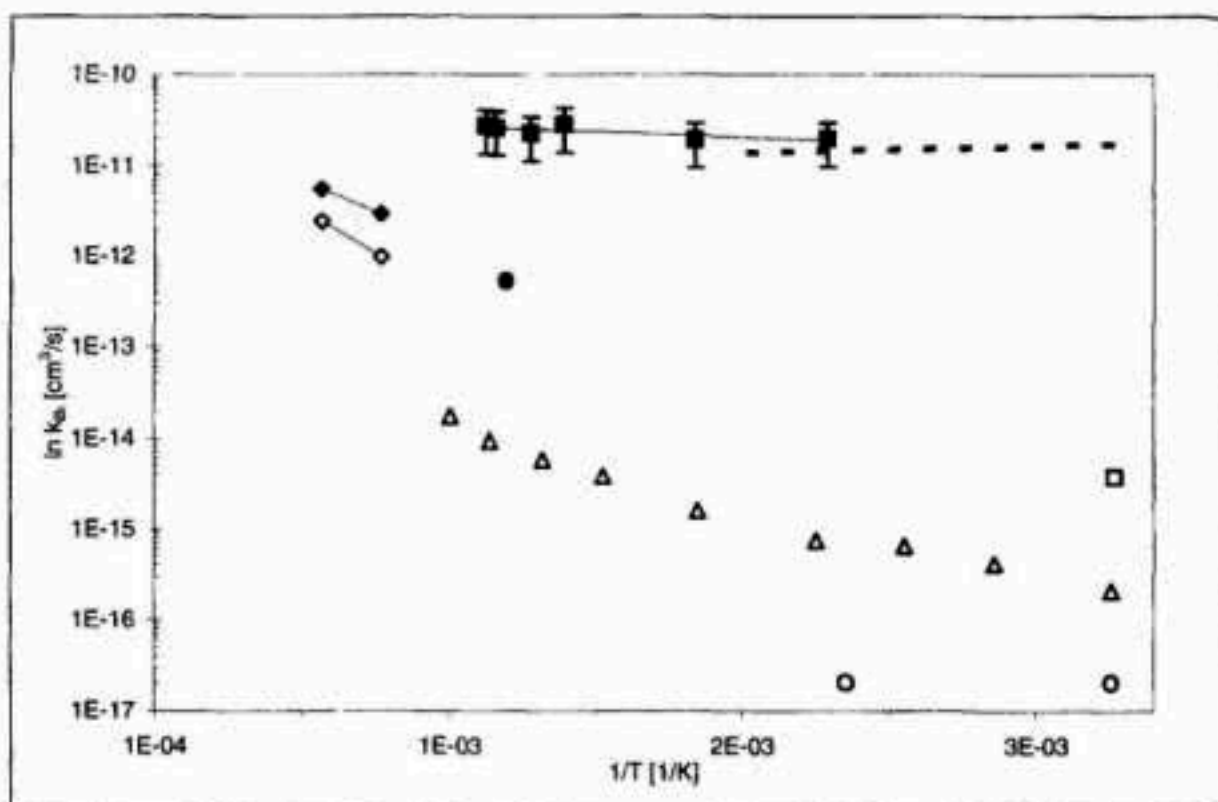


Figure 9. Arrhenius plot for the reaction $\Phi+O_2$. Solid squares: this work. Dashed line: Yu and Lin /3/. Solid diamonds: Phenoxy channel, Frank et al. /4/. Open diamonds: Paraquinone channel, Frank et al. /4/. Solid circle: Baldwin et al. /8/. Open squares: Yu and Lin /2/. Open triangles: Möhlenbrock /7/. Open circles: Preidel and Zellner /6/.

temperature dependence, however, seems to be different from that of Yu and Lin. In Arrhenius form we obtain:

$$k_{2ox} = 3.8 \times 10^{-11} \exp(-290/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}.$$

This expression is only valid in the 400 to 800 K temperature regime. An extrapolation, in particular to higher temperatures, is unwise since here k_{2ox} is composed of several channel rate coefficients each of which is strongly temperature dependent (see discussion).

DISCUSSION

Several features help to minimize undesired subsequent reactions:

- Our radical source is relatively clean releasing only small amounts of the precursor into the system.
- The rate coefficients for our primary processes (i.e. reactions with NO or O_2) are large ($>10^{11}$ $\text{cm}^3/\text{molec sec}$).
- Our initial radical concentrations are low ($<10^{11}$ cm^3 at the start of the measurement).

Rate Coefficients for the Fast Reactions of Phenyl Radicals

As a result we work with virtually isolated kinetic conditions and our measured rate coefficients need not be subjected to kinetic corrections.

For the reaction $\Phi + \text{NO}$ three direct determinations exist at present, using different methods. In all of these studies phenyl profiles were measured in an excess of NO to obtain the rate coefficient of the entrance channel. In addition, Yu and Lin /1/ showed that at the lower temperatures pressure effects are small. Consequently, the data of the three groups may be directly compared. The good agreement in particular between our data and those of Yu and Lin /1/ gives confidence in our mass spectrometric method which has been applied to direct phenyl measurements for the first time. The fall off which has been observed is discussed below.

With $\Phi + \text{O}_2$, our rate coefficients are the first ones obtained from phenyl decays and show that this reaction is in fact very rapid at lower temperatures as well as at higher temperatures. This supports Yu and Lin's /3/ assumption that the earlier studies were in error; presumably due to a problem associated with the method of optical measurement used.

One may assume that at moderate temperatures collisional stabilization is the only accessible product channel and we failed to detect products from other channels with the mass spectrometer. In this case our $k_{2\text{tot}}$ (entrance channel) should coincide with Yu and Lin's $k_{2\text{stab}}$ and this is indeed found in the overlapping temperature region of the two studies.

Although this underlines the unexpectedly large role of the stabilization channel we unfortunately failed to detect ΦOO signals in our mass spectrometer. This is not too surprising because of the combination of our low Φ concentrations with the notoriously low mass spectrometric sensitivities for peroxy radicals.

What we found were phenol product profiles indicating that ca. 10 % of the excited $(\Phi\text{OO})^*$ molecules are lost into this channel. At present we assume that this is the result of a heterogeneous reaction.

At the high temperature side of our measurements we still have interpretation problems and here definitely more work is needed. The collisional channel should drop at higher temperatures in accord with the rate constant calculations of Yu and Lin /3/. This is not reflected by the temperature dependence of our $k_{2\text{tot}}$ nor do we find a significant pressure effect within our limited pressure range. The pressure effect is more pronounced at higher temperatures and we intend to go up to about 1000 K. This, however, requires a different Φ source, probably ΦI .

In addition, by making a study of the products of the high temperature reaction it should be possible to determine the relative importance of the different high temperature channels i.e. ΦO and $\text{C}_6\text{H}_4\text{O}_2$. Furthermore, such a study may reveal products which have so far not been detected which may be indicative of new high temperature channels. This will help to clarify the interplay between the fall-off of $k_{2\text{stab}}$ and the increasing importance of k_{2a} and k_{2b} .

FALL OFF EFFECTS FOR $\Phi + \text{NO}$ AND $\Phi + \text{O}_2$

For the reaction $\Phi + \text{NO}$ there is clearly a fall off in the rate coefficient with increasing temperature (fig 6). A comparison between the experimental data and the calculated fall

Transport Phenomena in Combustion, Volume 1

off curve for 0.7 mbar shows that there is good agreement below 500 K but at higher temperatures there is increasingly poorer agreement. The theoretical fall off curves were obtained from Troe calculations /17/. An experiment was performed at 10.6 mbar, the highest pressure currently achievable in our reactor, and 800 K. In this case there is good agreement with the appropriate fall off curve. We currently believe that a fraction of the excited Φ NO radicals is stabilised at the walls; which may be assumed to occur with unit efficiency. Thus the stabilisation of the excited Φ NO radicals is a combination of homogenous (gas phase) and heterogenous (wall) reactions. The effect of the wall is a diffusion controlled process and will be less significant at high pressures or low temperatures and under these conditions the rate data represent the gas phase stabilisation. Conversely, at high temperatures and low pressures diffusion to the walls is larger and the reactor is acting partly like a VLPP reactor and the measured rate coefficients are shifted towards k^{∞} . Indeed for our reactor geometry a mean free path calculation shows that at 0.7 mbar and 800 K a molecule will undergo 2 effective collisions before reaching the walls assuming a collision efficiency of 10^{-2} /18/. Whereas at 10.6 mbar and 800K it would undergo 30 effective collisions. To define the fall off curve experimentally more measurements are being made at 10 mbar so that the apparent wall effects are minimised.

For $\Phi+O_2$ the same fall off effects at low pressures and high temperatures should be observed as for $\Phi+NO$. However we have observed no fall off at all. As a preliminary explanation we assume that the high temperature channels are less temperature dependant than deduced in the earlier study /4/ and that they are thus more accessible below 1000 K. In order to reduce any wall effects more measurements need to be made of this reaction at higher pressures.

CONCLUSION

The kinetics of Φ radicals were studied for the first time by monitoring Φ directly with a mass spec and the method was validated by the reaction $\Phi+NO$ below 500K. At higher temperatures a marked fall off in the rate coefficient has been observed. For $\Phi+O_2$, rate coefficients were obtained which are several orders of magnitude higher than earlier results deduced from Φ absorption measurements. The results of the present study are in good agreement with data recently obtained from product rise times by Yu and Lin. This shows the importance of the stabilization channel at intermediate temperatures. More work is required at higher temperatures and pressures to avoid the wall effects observed in the $\Phi+NO$ reaction.

Rate Coefficients for the Fast Reactions of Phenyl Radicals

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