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THE KINETICS OF THE REACTIONS OF 2,6-DI-t-BUTYL-4-METHYLPHENOL AND 2,4,6-TRIMETHYLPHENOL WITH NITROGEN DIOXIDE IN SOLUTION

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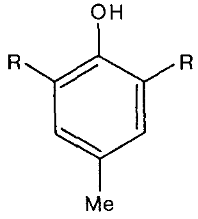
Abstract:- The reaction of 2,6-di-t-butyl-4-methylphenol with nitrogen dioxide to form 2,6-di-t-butyl-4-methyl-4-nitrocyclohexa-2,5-dienone has a first order dependence of rate on the concentration of the species N_2O_4. By contrast the observed rate of the corresponding reaction of 2,4,6-trimethylphenol is independent of the concentration of nitrogen containing species.

It has been reported previously[1] that nitrogen dioxide reacts with 2,6-di-t-butyl-4-methylphenol (1.a) in petroleum spirit over 2 h at room temperature in the absence of air to form 2,6-di-t-butyl-4-methyl-4-nitrocyclohexa-2,5-dienone (2.a). Further reaction over 6 h yielded the cyclohexenone (3) in low yield. A free radical mechanism was proposed for the first stage of this reaction involving the phenoxy radical formed by hydrogen atom abstraction from (1.a) by the species $NO_2^{\cdot}$.



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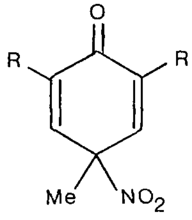

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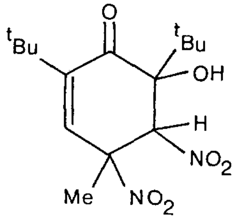

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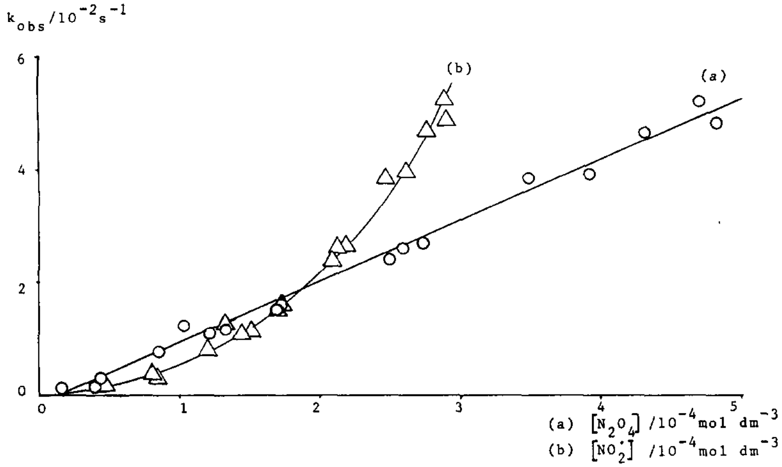
(a) R = ^{t}Bu
(b) R = Me

We now wish to report the results of a kinetic study of the first stage of this reaction and of the related reaction of (1.b). Product studies confirmed the original report and also showed that (3) was formed from (2.a) not only by further reaction with nitrogen dioxide but also by the decomposition of (2.a), which gave (3) together with (1.a). Kinetic studies of the initial reaction were carried out over a range of temperatures in cyclohexane. The nitrogen dioxide is present as a rapidly equilibrating mixture of $NO_2^{\bullet}$ and N_2O_4 and values of the equilibrium constant are known[2]. Reactions were performed with the nitrogen dioxide in an excess (with $[N_2O_4] + \frac{1}{2}[NO_2^{\bullet}]$ in the range 1×10^{-5} – 5×10^{-4} mol dm^{-3} and with (1.a) in the range (10^{-6} – 5×10^{-5} mol dm^{-3}) and were followed by U.V. spectrophotometry, the extinction curves having an isosbestic point at 263 nm. Good first order kinetic plots yielding rate coefficients, k_{obs}, were observed when allowance was made for the subsequent slow decomposition of (2.a). Values of k_{obs} at 298 K are shown in the Figure, (a) plotted against $[N_2O_4]$, and (b) plotted against $[NO_2^{\bullet}]$.



FIGURE

It is clear that there is not a first order dependence of rate on $[NO_2^{\bullet}]$ but that k_{obs} α $[N_2O_4]$. Further studies were performed over the temperature range 283-336 K and at each temperature this relationship was obeyed.

These results could be accommodated in terms of the free radical mechanism only if the first stage were a rapid pre-equilibrium and reaction of the phenoxyl radical with $NO_2^{\bullet}$ was rate limiting. There are recent precedents for such a process being the rate limiting one of a reaction sequence[3]. This would lead to the equation rate α $[NO_2^{\bullet}]^2$, and is consistent with the experimental observations as $[N_2O_4]$ α $[NO_2^{\bullet}]^2$. Values of the third order rate coefficients, $k_3 = k_{obs}/[NO_2^{\bullet}]^2$, at various temperatures are, however, given in Table 1. A negative temperature coefficient of reaction rate (E_{ACT} = -33 kJ mol^{-1}) results from these data. Neither step in the free radical mechanism would be expected to contribute to such a result. The reaction of $NO_2^{\bullet}$ with a complex of (1.a) with $NO_2^{\bullet}$ formed reversibly in small amount[4] would provide a possible explanation of the kinetic results, if the complex were formed with a negative enthalpy of reaction.

An alternative interpretation would involve a rate limiting reaction between (1.a) and N_2O_4 or some species (other than $NO_2^{\bullet}$) in equilibrium with N_2O_4. The appropriate second order rate coefficients, $k_2 = k_{obs}/[N_2O_4]$, are also given in Table 1, and the activation energy is 28 kJ $mole^{-1}$. Reactions were also studied at higher temperatures (in heptane) in an attempt to see if there was a contribution to the rate from a reaction first order in $NO_2^{\bullet}$. Such a reaction was detectable above about 342 K and at that temperature the component of reaction first order in $NO_2^{\bullet}$ gave a second order rate coefficient of 3 dm^3 mol^{-1} s^{-1} indicating its relative insignificance (cf. Table 1).

Table 1

Variation of Rate Coefficients with Temperature (T)

T/K	$k_3/10^{-5}$ dm^6 mol^{-2} s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
283	12	59
293.5	8	100
298	6	108
310	4	180
321	3	260
326	2	320
331	1	298
336	1	400

2,4,6-Trimethyl-4-nitrocyclohexa-2,5-dienone (2.b) may be prepared in 88% yield by reaction of nitrogen dioxide with 2,4,6-trimethylphenol (1.b). Further reaction with nitrogen dioxide occurs more slowly to produce adducts apparently analogous to (3). However, in surprising contrast to (2.a), (2.b) rearranges slowly at room temperature and rapidly and quantitatively in carbon tetrachloride under reflux to give 2,6-dimethyl-4-nitromethylphenol. This interesting transformation has been noted previously[5].

The kinetics of the reaction of (1.b) were studied in cyclohexane at 298 K with the results shown in Table 2. In marked contrast to that of (1.a), the reaction rate is effectively independent of the concentration of N_2O_4

(or $NO_2^{\bullet}$). This behaviour could be explained by an initial rapid reaction resulting in an intermediate species which then reacts slowly to form (2.b). The speed of the reactions, which were followed by stopped-flow spectrophotometry, precludes the accurate determination of the ultraviolet spectrum of this species. It is apparent, however, that the intermediate must have absorptions not too dissimilar to those of the phenol at 240 nm and 280 nm. The difference in behaviour of (1.a) and (1.b) may be due to the steric hindrance offered by the t-butyl groups of (1.a) to the first stage of the reaction.

Table 2

Rates of Reaction of 2,4,6-Trimethylphenol† with Nitrogen Dioxide at 298 K

$[N_2O_4]/10^{-3}$ mol dm^{-3}	k_{obs}/s^{-1}
0.06	0.104
0.21	0.108
0.41	0.109
0.68	0.113
0.94	0.115
1.24	0.119
1.41	0.116

†[2,4,6-Trimethylphenol] = 1.0×10^{-5} mol dm^{-3}

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