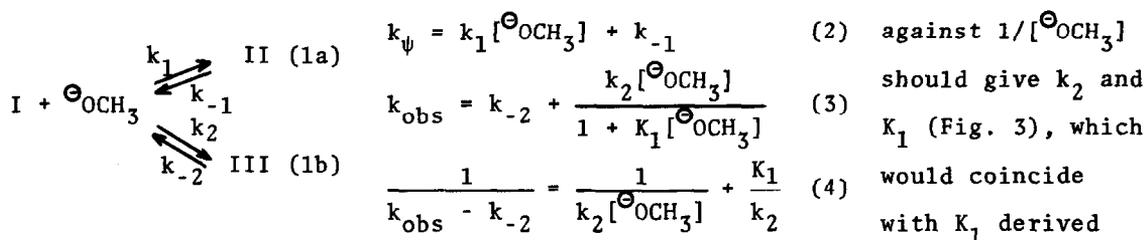AROMATIC NUCLEOPHILIC SUBSTITUTION VIII.[1] STOPPED-FLOW KINETICS OF THE

TRANSIENT 1,3-DISUBSTITUTED ANIONIC σ COMPLEX IN THE REACTION OF

1-PIPERIDINO-2,4-DINITRONAPHTHALENE WITH POTASSIUM METHOXIDE

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Ever since Servis[2] first observed by NMR spectrometry that in DMSO much

faster formation of 1,3-disubstituted anionic σ complex (hereinafter referred

to as 1,3-adduct) from 2,4,6-trinitroanisole (TNA) and $^{\ominus}OCH_3$ is followed by a

much slower attack on the 1-position, considerable attention has been directed

toward 1,1-(corresponding to Meisenheimer complex) and 1,3-adducts.[3] As for

isomeric 1,3-adducts formed in the reaction of aromatic substrates bearing two

activating groups with bases, there have so far been few studies. Previous

work has been limited to such 1,3-adducts as formed in the reactions of benzene

derivatives activated by three electron-attracting groups such as TNA with

bases.[3] Replacement of a benzene- with a naphthalene-ring, however, could make

such 1,3-adducts bearing two activating groups stable enough to be confirmed,

which is the case with the 1,3-adduct (II) from 1-piperidino-2,4-dinitronaphth-

alene (I) and $KOCH_3$ in DMSO-CH_3OH (eqn 1).[4] Fig. 1 shows the spectral change

relevant to the interaction of I with $KOCH_3$ in DMSO-CH_3OH. Curve d is

attributable to the 1,3-adduct, which was obtained by plotting the absorbance

at infinity at each wavelength by means of a stopped-flow spectrophotometric

method (SFSM), and curve c is characteristic of the 1,1-adduct (III).[4] The

first step is the attainment of equilibrium for II with the apparent rate

constant k_ψ, which is measured with a SFSM (eqns 1a and 2). k_1 and k_{-1}, and

thus K_1 are determined from a linear plot of k_ψ against $[^{\ominus}OCH_3]$ (eqn 2). The

second step is the much slower equilibrium formation of III with the apparent

rate constant k_{obs} (eqn 1b). Extrapolation to the intercept should give k_{-2}

(eqn 3 and Fig. 2). Once k_{-2} is obtained, the inversion plot of $1/(k_{obs} - k_{-2})$

$$\begin{array}{c} \xrightarrow{k_1} \quad \text{II} \quad (1a) \\[2pt] \text{I} + {}^{\ominus}\text{OCH}_3 \quad \overset{k_{-1}}{\rightleftharpoons} \\[2pt] \xrightarrow{k_2} \\ \xleftarrow{k_{-2}} \quad \text{III} \quad (1b) \end{array}$$

$$k_\psi = k_1[{}^{\ominus}\text{OCH}_3] + k_{-1} \qquad (2)$$

$$k_{obs} = k_{-2} + \frac{k_2[{}^{\ominus}\text{OCH}_3]}{1 + K_1[{}^{\ominus}\text{OCH}_3]} \qquad (3)$$

$$\frac{1}{k_{obs} - k_{-2}} = \frac{1}{k_2[{}^{\ominus}\text{OCH}_3]} + \frac{K_1}{k_2} \qquad (4)$$

against $1/[{}^{\ominus}\text{OCH}_3]$ should give k_2 and K_1 (Fig. 3), which would coincide with K_1 derived from eqn 2. Table 1 shows the difference in K_1 (520±45 and 311±52 at 25°) is a little larger than expected. Although whether the conversion of II to III takes place by the direct route II→III or by the route II→I→III is a question which kinetic measurements can not answer, the direct route might substantially be responsible for it.[3b] k_{-2} are considered to be inaccurate as seen from their experimental errors, because extrapolation to the intercept is arbitrary to some extent (Fig. 2), so the $\Delta H^{\ddagger}_{-2}$, $\Delta S^{\ddagger}_{-2}$, ΔH, ΔS, and K_2 become equivocal to that extent. Trial calculation shows that K_2 is $(3.1\pm2.4)\times10^4$, $(7.7\pm3.8)\times10^3$, and $(4.1\pm0.6)\times10^3$ at 25, 35, and 40°, respectively. Multiple alkoxy-substitution has a large stabilizing effect on a sp^3 carbon as well as relative to an equally substituted sp^2 carbon.[3a,5] In I, therefore, the piperidyl group at the 1-position in the place of an alkoxyl group is considered to make III less stable than a 1,1-dialkoxy-substituted adduct, which thus rendered the kinetics of both adducts formation possible, together with the replacement of a benzene- with a naphthalene-ring.[4b] The detailed study is now in progress.

References

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Y. Ando, Bull. Chem. Soc. Jpn., 49, 1451 (1976).

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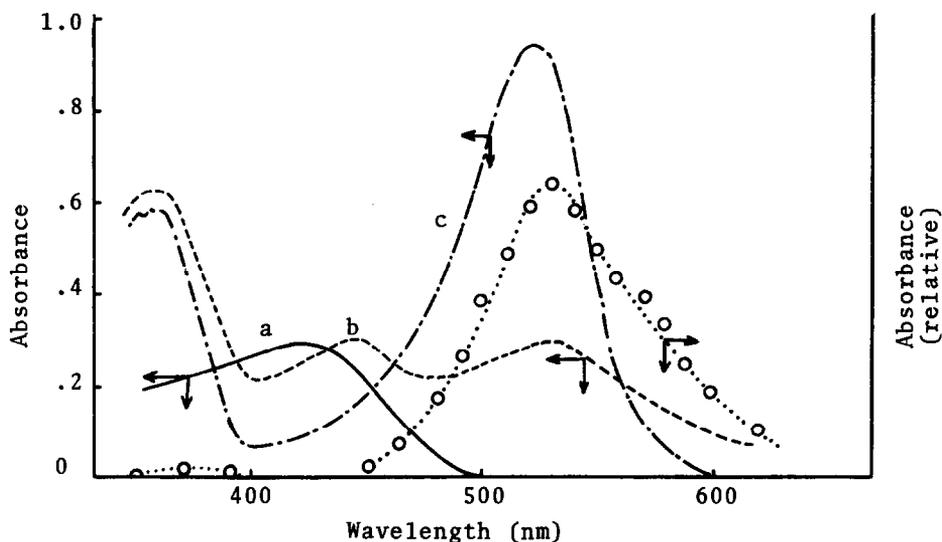   Mahone, and C. L. Liotta, ibid., 89, 5911 (1967).

Fig. 1   Spectral changes relevant to the reaction of 1-piperidino-2,4-dinitronaphthalene with $KOCH_3$ in CH_3OH-DMSO (1:9, v/v); a I (3.5×10^{-5} $mol\cdot l^{-1}$) before addition of $KOCH_3$; b and c immediately and 60 min after addition of $KOCH_3$ (8.2×10^{-3} $mol\cdot l^{-1}$); d obtained by means of a stopped-flow method (I 7.0×10^{-4} $mol\cdot l^{-1}$); CH_3OK 3.9×10^{-3} $mol\cdot l^{-1}$).
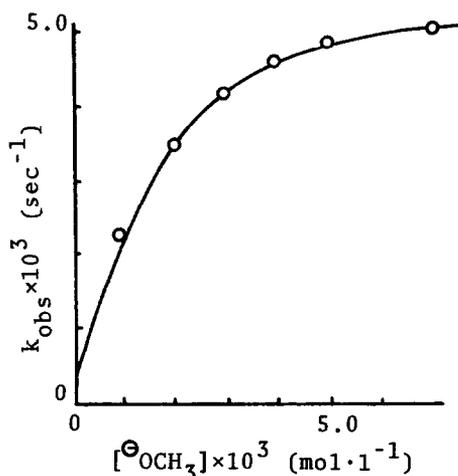
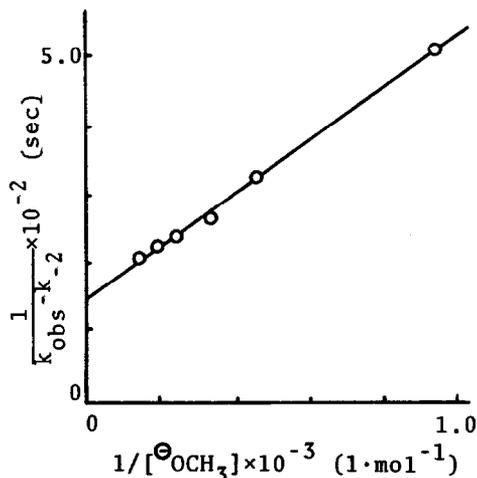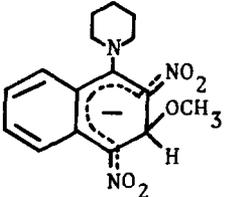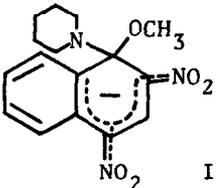Fig. 2   Relationship between k_{obs} and [$^{\ominus}OCH_3$].

Fig. 3   Relationship between $1/(k_{obs}-k_{-2})$ and $1/[^{\ominus}OCH_3]$.

Table 1   Kinetic and thermodynamic data on the formation of the 1,3- and 1,1-adducts.

II   III

$k_1 (l \cdot mol^{-1} \cdot sec^{-1})$	15°	$2.36\pm0.04\times10^2$	$k_2 (l \cdot mol^{-1} \cdot sec^{-1})$	25°	2.53 ± 0.29
	25°	$4.92\pm0.21\times10^2$		35°	5.22 ± 0.57
	35°	$9.49\pm0.49\times10^2$		40°	7.27 ± 0.35
$k_{-1} (sec^{-1})$	15°	0.38 ± 0.02	$k_{-2} (sec^{-1})$	25°	$1.8\pm1.3\times10^{-4}$
	25°	0.95 ± 0.04		35°	$8.5\pm3.5\times10^{-4}$
	35°	2.05 ± 0.13		40°	$1.8\pm0.2\times10^{-3}$
$K_1 (l \cdot mol^{-1})$	15°	627 ± 38	$K_1 (l \cdot mol^{-1})$	25°	311 ± 52
	25°	520 ± 45		35°	241 ± 38
	35°	465 ± 53		40°	239 ± 18
$\Delta H^{\ddagger}_1 (kcal \cdot mol^{-1})^c$		11.5	$\Delta H^{\ddagger}_2 (kcal \cdot mol^{-1})^c$		12.2 ± 1.9
$\Delta H^{\ddagger}_{-1} (kcal \cdot mol^{-1})^c$		14.1	$\Delta H^{\ddagger}_{-2} (kcal \cdot mol^{-1})^c$		27.2 ± 13.0
$\Delta S^{\ddagger}_1 (e.u.)^c$		-7.6	$\Delta S^{\ddagger}_2 (e.u.)^c$		-15.4 ± 6.4
$\Delta H (kcal \cdot mol^{-1})^c$		-2.6	$\Delta H (kcal \cdot mol^{-1})^c$		-15.0
$\Delta S (e.u.)^c$		3.7	$\Delta S (e.u.)^c$		-31.2

[a] Rate constants were calculated from the kinetics of the formation of the 1,3-adduct by means of a SFSM.

[b] Rate constants were calculated from the kinetics of the formation of the 1,1-adduct.

[c] At 25°.