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Superacids and Their Derivatives. III.[1] Kinetics of the Oxonium Ion Formation from Superacid Esters and Tetrahydropyran. Oxonium-Ester Equilibria

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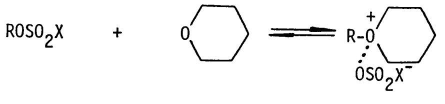
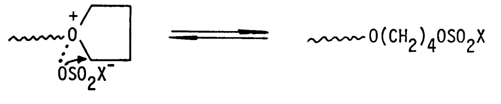
Kinetic studies on the oxonium formation reaction between superacid esters ($ROSO_2X$) and tetrahydropyran (THP) were carried out by means of NMR spectroscopy. The reaction was found to be an equilibrium process.



The rate constant (k) of S_N2 reaction and the equilibrium constant ($1/K = k/k'$) were determined. The solvent effect was examined and k was found to be in the order: nitrobenzene>chlorobenzene≈CH_2Cl_2>liquid SO_2. The effects of R and X in $ROSO_2X$ were studied. Relative reactivities of primary alkyl series in the reaction of $ROSO_2Cl$ with THP were: Me: Et: n-Pr=4.63: 1.0: 0.294 in CH_2Cl_2 and Me: Et: n-Pr=3.19: 1.0: 0.452 in nitrobenzene. The effect of X on k was in the order Cl≈CF_3>F, the $1/K$ value being also extremely low when X=F. The result was discussed in relation to the kinetics of the polymerization of tetrahydrofuran (THF) by $ROSO_2X$.

We have found that superacid esters[2] and anhydrides[1] are very effective initiators for the cationic ring-opening polymerization of tetrahydrofuran (THF). Kinetic studies on the THF polymerization with a superacid ester initiator revealed that the propagating species was predominanantly a cyclic oxonium one (**1**), and that the concentration of ester type species (**2**) was very small although the latter might be in equilibration with the former species under the polymerization conditions as shown in the following. In fact, **2** could not be detected during the THF polymerization in CH_2Cl_2 by means of high resolution NMR spectroscopy.[2] Thus it is importantto examine the oxonium-ester equilibrium in more detail by independent reactions. Although it is known that a superacid ester such as ethyl fluorosulfate ($EtOSO_2F$) reacts with ether to form an oxonium ion,[3] no quantitative study on the oxonium formation reactions from superacid esters has been carried out so far.[4]

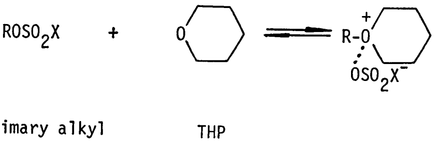


(1)

1 2

(X=Cl, F, CF3)

In the present study reactions of superacid esters with tetrahydropyran (THP) were examined as a model system, as shown in the following. Superacid esters examined were primary alkyl esters of chlorosulfonic ($ROSO_2Cl$), fluorosulfonic ($ROSO_2F$) and trifluoromethanesulfonic ($ROSO_2CF_3$) acids.



(2)

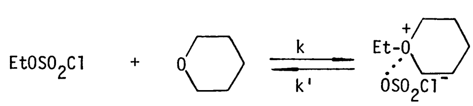
R=primary alkyl THP
X=Cl, F, CF3

THP was employed as an ether component since THP is an ether of high basicity[5] and has no ring-opening polymerizability.[6] The reaction corresponds to the initiation of the cyclic ether polymerizations by superacid ester initiators.[2] Kinetic analysis was carried out by direct determination of the instantaneous concentrations of THP and the product oxonium ion by means of NMR spectroscopy. Thus, the reaction was found to be characterized by a reversible reaction, *i.e.*, the ester and oxonium species are in equilibration. We have also studied the effects of the nature of R and X in $ROSO_2X$ as well as those of solvents on the reaction rate (k) and equilibrium constant ($1/K$).

Results and Discussion

Determination of Reaction Rates. Figure 1 shows an NMR spectrum of the reaction system of $EtOSO_2Cl$ with THP in CH_2Cl_2 at a reaction time of 124 min at 35 °C. Signal assignments are given in Table 1.

The following relationships are given for the concentration of the respective component:



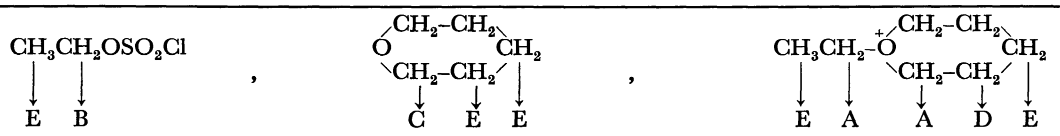
(3)

3

at time 0	$[E]_0$	$[T]_0$	—
at time t	$[E]_0-[Ox]$	$[T]_0-[Ox]$	$[Ox]$

where $[E]_0$ and $[T]_0$ denote the initial concentrations of $EtOSO_2Cl$ and THP, respectively, [Ox] denotes the concentration of the product, cyclic oxonium, and k and k' denote the rate constants of the oxonium formation reaction and the reverse reaction, respectively. The stoichiometry of (3) was shown to be valid by the areas of the respective peaks on the basis of that of the internal standard $CHCl_3$ (Table 1). From the signal (peak D) of the β-methylene protons of the cylic oxonium, the [Ox] *vs.* time relationship was obtained (Fig. 2). The rate equation of the oxonium formation of (3) is given by

TABLE 1. SIGNAL ASSIGNMENTS IN THE REACTION OF $EtOSO_2Cl$ WITH THP IN CH_2Cl_2 AT 35 °C AND INTEGRAL VALUES



Signal	Chemical shifts in ppm[a]	Integral value
A	4.9—4.7 (m)	$6Ox+2(E_0-Ox)=2E_0+4Ox$
B	4.60 (q)	
C	3.6 (m)	$4(T_0-Ox)=4T_0-4Ox$
D	2.0 (m)	$4Ox$
E	1.8—1.3 (m)	$3(E_0-Ox)+6(T_0-Ox)+5Ox=3E_0+6T_0-4Ox$
$CHCl_3$	7.30 (s)	S_0

a) Calculated from the chemical shift of $CHCl_3$ as δ 7.30. Multiplicity: m=multiplet, q=quartet and s=singlet

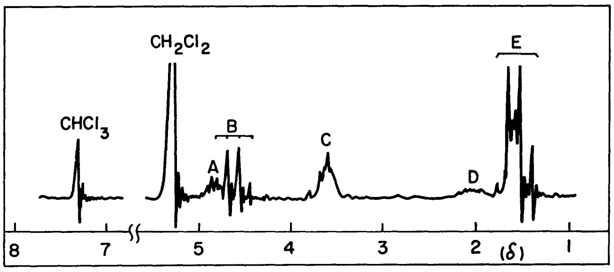


Fig. 1. NMR spectrum of the reaction system of $EtOSO_2Cl$ with THP in CH_2Cl_2 after 124 min at 35 °C. $[E]_0=0.822$ mol/l, $[T]_0=0.835$ mol/l, $CHCl_3$: an internal standard.

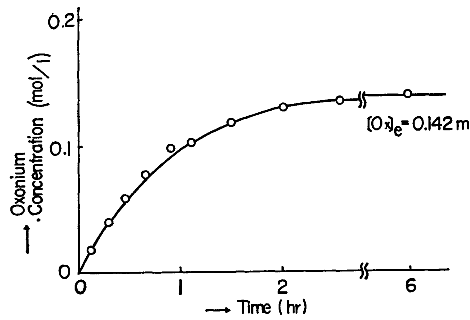


Fig. 2. Time-conversion curve of the reaction of $EtOSO_2Cl$ with THP at 35 °C in CH_2Cl_2. $[E]_0=0.822$ mol/l, $[T]_0=0.835$ mol/l.

$$\frac{d[Ox]}{dt} = k([E]_0-[Ox])([T]_0-[Ox]) - k'[Ox], \qquad (4)$$

and the equilibrium constant of (3), $1/K$, is defined by

$$\frac{1}{K} = \frac{k}{k'} = \frac{[Ox]_e}{([E]_0-[Ox]_e)([T]_0-[Ox]_e)} \qquad (5)$$

where $[Ox]_e$ is the concentration of the cyclic oxonium at equilibrium which can be obtained from Fig. 2. Equation (4) is then transformed by using Eq. (5) into

$$\frac{d[Ox]}{dt} = k\{[Ox]^2-(K+[E]_0+[T]_0)[Ox]+[E]_0[T]_0\} \qquad (6)$$

By introducing α and β, which are two roots of the equation $X^2-(K+[E]_0+[T]_0)X+[E]_0[T]_0=0$, Eq. (6) becomes

$$\frac{d[Ox]}{dt} = k([Ox]-\alpha)([Ox]-\beta) \qquad (7)$$

where

$$\alpha = \frac{1}{2}\left\{K+[E]_0+[T]_0+\sqrt{(K+[E]_0+[T]_0)^2-4[E]_0[T]_0}\right\}$$
$$\beta = \frac{1}{2}\left\{K+[E]_0+[T]_0-\sqrt{(K+[E]_0+[T]_0)^2-4[E]_0[T]_0}\right\} \qquad (8)$$

Integrating (7) from t_1 to t_2 and $[Ox]_1$ to $[Ox]_2$, we have

$$k = \frac{2.303}{(\alpha-\beta)(t_2-t_1)} \log \frac{(\beta-[Ox]_1)(\alpha-[Ox]_2)}{(\alpha-[Ox]_1)(\beta-[Ox]_2)} \qquad (9)$$

The $1/K$ value could be obtained from $[Ox]_e$ value (Fig. 2) according to Eq. (5). Thus the values of α and β of Eq. (8) were calculated. In the $EtOSO_2Cl$–THP system at 35 °C in CH_2Cl_2, $1/K$ value was 0.301 l/mol, and k was then obtained by Eq. (9): $k=7.80 \times 10^{-5}$ l/mol·s at 35 °C in CH_2Cl_2.

Similarly, kinetic analysis was carried out with other superacid esters in CH_2Cl_2 and liquid sulfur dioxide (SO_2) solvents. In nitrobenzene and chlorobenzene solvents, however, no internal standard was used; instead, these solvents were used as standards for integration. The reactions in these four solvents were homogeneous throughout the kinetic runs. Kinetic runs were carried out at 35 °C and dataare summarized in Table 2.

Reaction Mechanism. The reaction of THP with superacid esters (Eq. (2)) is a dipole-dipole reaction to produce an onium salt. It is interesting to compare Eq. (2) with the Menschutkin reaction, which is also a dipole-dipole reaction between amine and alkyl halide to produce an ammonium salt (Eq. (10)).

$$RY + R_3'N \longrightarrow RR_3'\overset{+}{N}\overset{-}{Y} \qquad (10)$$

Since the Menschutkin reaction is not reversible[9] the present reaction of (2) is characterized by equilibrium process.

Kinetic runs of the $EtOSO_2Cl$–THP reaction (3) were carried out in CH_2Cl_2 and nitrobenzene at various temperatures. Arrhenius plots were linear in both cases, and activation parameters were obtained (Table 3). The reaction was faster in nitrobenzene than in CH_2Cl_2. $\Delta H^{\ddagger}$ values 14.4 and 15.2 kcal/mol are relatively low for a bimolecular reaction (favorable for k), whereas $\Delta S^{\ddagger}$ values, −31 and −26 e.u., are also low (unfavorable for k). It is typical for a dipole-dipole reaction to form ionic species. These values of activation

TABLE 2. KINETIC DATA OF THE REACTIONS OF THP WITH SUPERACID ESTERS AT 35 °C

Run No.	$ROSO_2X$ X	$ROSO_2X$ R	Solvent (ε)[a]	$1/K$ (l/mol)	$10^5 \cdot k$ (l/mol·s)
1	Cl	Me	CH_2Cl_2 (8.93)[b]	2.68	36.1
2	Cl	Et	CH_2Cl_2	0.301	7.80
3	Cl	*n*-Pr	CH_2Cl_2	0.258	2.29
4	Cl	Me	$C_6H_5NO_2$ (34.8)	5.29	79.0
5	Cl	Et	$C_6H_5NO_2$	1.40	24.8
6	Cl	*n*-Pr	$C_6H_5NO_2$	0.756	11.2
7	Cl	Et	C_6H_5Cl (5.94)[b]	0.480	9.37
8	Cl	Et	SO_2 (12.4)[c]	2.15[d]	1.22[d]
9	F	Me	CH_2Cl_2	0.412	12.4
10	F	Et	CH_2Cl_2	0.070	2.43
11	F	Me	$C_6H_5NO_2$	3.60	70.1
12	F	Et	$C_6H_5NO_2$	0.805	24.1
13	CF_3	Et	CH_2Cl_2	0.177	6.10
14	CF_3	Et	$C_6H_5NO_2$	0.733	27.3

a) Dielectric constant at 25 °C. b) Taken from Ref. 7. c) Taken from Ref. 8. d) Data at 20 °C.

TABLE 3. KINETIC DATA AND ACTIVATION PARAMETERS IN THE REACTION OF $EtOSO_2Cl$ WITH THP[a]

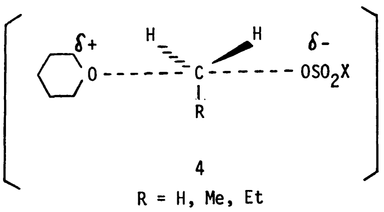
	In CH_2Cl_2	In nitrobenzene
$10^5 \cdot k$(l/mol·s)	2.51 ($1/K$=0.595, 20 °C)	6.01($1/K$=1.70, 18 °C)
	5.56 ($1/K$=0.476, 30 °C)	10.9 ($1/K$=1.60, 29 °C)
	7.80 ($1/K$=0.301, 35 °C)	24.8 ($1/K$=1.40, 35 °C)
	17.0 ($1/K$=0.175, 42 °C)	55.9 ($1/K$=1.08, 44 °C)
$\Delta H^{\neq}$ (kcal/mol)	14.4	15.2
$\Delta S^{\neq}$ (e.u.)	−31	−26

a) $1/K$ in l/mol.

parameters are very close to those of the Menschutkin reaction, *e.g.*, $\Delta H^{\neq}=13.0$ kcal/mol and $\Delta S^{\neq}=-29$ e.u. in the reaction of pyridine with methyl iodide in nitrobenzene.[10)]

(11)

Thus the transition state of Eq. (2) may be formulated in a similar way to the Menschutkin reaction.[9)]



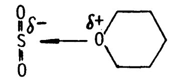
4

R = H, Me, Et

In the reaction of $EtOSO_2Cl$ with THP, $1/K<1$ in CH_2Cl_2 but $1/K<1$ in nitrobenzene in the temperature range examined (Table 3). The temperature rise led to a decrease in $1/K$ values, *i.e.*, oxonium formation is thermodynamically favored at lower temperatures. It should be added that no side reactions were observed in all the kinetic runs.

Solvent Effects. As seen from Tables 2 and 3 the rates (k) were in the order nitrobenzene>chlorobenzene≈CH_2Cl_2>liquid SO_2. This order can not be simply explained by the solvent polarity because it is not in line with the order of dielectric constants (Table 2): nitrobenzene>liquid SO_2>CH_2Cl_2>chlorobenzene. Since the solvents are of different character they may have complicated effects. It can be said that the reaction is faster in more polar solvents as in the case of the Menschutkin reaction.[7)] In aromatic solvents, k in nitrobenzene is 2.6 times as high as that in chlorobenzene at 35 °C. This can be compared with the reactivity in the Menschutkin reaction of Eq. (11), in which the rate was 9.3 times as high as that in chlorobenzene.[10)]

In liquid SO_2 at 20 °C, k was 5.3 times smaller than in nitrobenzene (calculated value of $k=6.50\times10^{-5}$ l/mol·s at 20 °C). A similar observation was also noted in the above Menschutkin reaction.[11)] A decreased reactivity in liquid SO_2 may be attributed to the solvation of THP at the initial state (**5**) as an interaction of amine with liquid SO_2.[11)] The complex formation of **5** is not unreasonable, because it is known that equilibrium constants are significantly large in the formation of complexes between SO_2 and alcohol.[12)]



5

It may be significant to compare activation parameters of the $EtOSO_2Cl$–THP reaction in CH_2Cl_2 and in nitrobenzene. Although k was larger in nitrobenzene, the $\Delta H^{\neq}$ value was also larger in it, *i.e.*, an increased reactivity is ascribed to the more favorable entropy factor in nitrobenzene. A similar result was observed in the Menschutkin reaction of Eq. (11), in

TABLE 4. SOLVENT EFFECTS ON Eqs. (2) AND (11)

Solvent	$10^5 \cdot k$ (l/mol·s)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$(e.u.)
C_2HCl_2	7.80^a	14.4	−31
C_6H_5Cl	9.37^a	—	—
$C_6H_5NO_2$	24.8^a	15.2	−26
C_6H_6	141^b	13.4	−34
$CHCl_3$	335^b	12.5	−35
C_6H_5Cl	398^b	13.2	−33
$C_6H_5OCH_3$	676^b	12.5	−34
$C_6H_5NO_2$	3720^b	13.0	−29

a) Present work of the reaction of Eq. (2). Data at 35 °C. b) Taken from Ref. 10. Data at 100 °C in the Menschutkin reaction of Eq. (11).

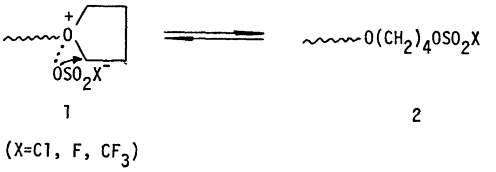
which an entropy factor ($\Delta S^{\neq}$) determines the reaction rate in various solvents irrespective of a slight change in $\Delta H^{\neq}$ values.[10] These solvent effects are compared and summarized in Table 4.

As to $1/K$ values of Eq. (2) the order of magnitude is roughly proportional to that of dielectric constants. The product oxonium ion is highly stabilized in solvents of high polarity. Among the solvents examined, liquid SO_2 is probably unique in the sense that it stabilizes the oxonium ion by electrophilic solvation of the counter-anion.[11]

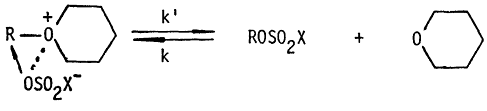
Effects of R and X in $ROSO_2X$. The rate of Eq. (2) depends upon the nature of R in $ROSO_2X$ (Table 2). The order of reactivities is Me>Et>*n*-Pr as seen in the other series of S_N2 reactions.[13] This order agrees with that of $1/K$ values in both CH_2Cl_2 and nitrobenzene.

Table 5 shows relative rates (Et=1.0) in several S_N2 reactions of dipole-dipole reactions (Nos. 1—5) like Eq. (2) and dipole-ion reactions (Nos. 6 and 7). The change of solvent (CH_2Cl_2 and nitrobenzene) had little effect on the relative reactivities (Nos. 1 and 2). A close resemblance of the relative rates, especially between reactions of Nos. 1, 2, 3, and 7, seems to indicate that the reactions proceed *via* a similar mechanism. The nature of X in $ROSO_2X$ also affects the rate. In the $EtOSO_2X$–THP reaction at 35 °C the order of reactivities is Cl≈CF_3>F in both CH_2Cl_2 and nitrobenzene solvents (Table 2). It should be noted that $1/K$ values are extremely low in the case of $ROSO_2F$.

Comparison of Eq. (2) with the THF Polymerization. It would be worth while to compare the reaction (2) with the THF polymerization initiated by superacid esters.[2] The equilibrium of Eq. (1) resembles rather the reverse reaction of Eq. (2) as given by Eq. (12).

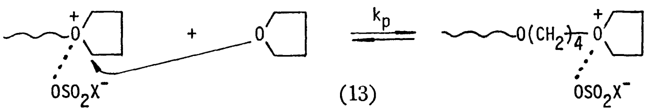


(1)



(12)

Both processes Eqs. (1) and (12) are intramolecular ones to produce ester type species. The products, however, are entirely different. In Eq. (1), the counter-anion of OSO_2X^- attacks the α-carbon of THF ring in the oxonium **1** to cause the ring-opening of THF. On the other hand, in Eq. (12) the counter-anion attacks alkyl group rather than α-carbon of the THP ring. In the propagation process of the THF polymerization (Eq. (13)), THF monomer attacks intermolecularly the α-carbon of THF ring in **1** instead of the intramolecular attack of the counter-anion of OSO_2X^-.

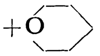
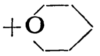
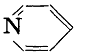


(13)

The existence of the oxonium-ester type equilibrium of Eq. (2) (or Eq. (12)) strongly suggests that the same type of equilibration (Eq. (1)) actually takes place during the course of THF polymerization. Such equilibration is very likely dependent upon the solvent since the present results of the solvent effect show remarkable changes of k and $1/K$ values of Eq. (2).

In a very recent presentation by Matyjaszewski *et al.*[19] the oxonium-ester equilibrium (Eq. (1)) has been discussed in the kinetic study of the THF polymerization by $EtOSO_2CF_3$ initiator. With a variation of polymerization solvents a wide range of apparent k_p values (2.0—23.0×10^{-3} l/mol·s, at 25 °C) have been obtained. They claimed that low apparent k_p values in non-polar solvents were due to a larger fraction of

TABLE 5. RELATIVE RATES OF SOME PRIMARY COMPOUNDS IN S_N2 REACTIONS

Reaction		Relative rate			Ref.
		Me	Et	*n*-Pr	
1. $ROSO_2Cl$+O 	in CH_2Cl_2 (35 °C)	4.63	1.0	0.294	This work
2. $ROSO_2Cl$+O 	in $C_6H_5NO_2$ (35 °C)	3.19	1.0	0.452	This work
3. $ROSO_2Cl+H_2O$	in dioxane (25 °C)	2.93	1.0	0.555	14)
4. $RI+Et_3N$	in acetone (100 °C)	11.4	1.0	0.19	15)
5. RI+N 	in $C_6H_5NO_2$ (25 °C)	18.7	1.0	—	16)
6. $RBr+EtO^-$	in ethanol (55 °C)	17.6	1.0	0.281	17)
7. $RI+PhO^-$	in ethanol (42.5 °C)	4.84	1.0	0.386	18)

the ester type **2** concentrations. However, no concentrations of oxonium **1** and ester **2** were determined in their kinetics.[19] For a quantitative argument further study of the oxonium-ester equilibria in detail is required.

Experimental

Materials. All the reagents were distilled under nitrogen. Methyl ($MeOSO_2Cl$), ethyl ($EtOSO_2Cl$) and *n*-propyl (*n*-$PrOSO_2Cl$) chlorosulfates were prepared by the reactions of sulfuryl chloride with the corresponding alcohols,[14] bp, $MeOSO_2Cl$, 51—52 °C/25 mmHg (lit.[14] 40 °C/14 mmHg), $EtOSO_2Cl$, 58 °C/25 mmHg (lit.[14] 42 °C/10 mmHg) and *n*-$PrOSO_2Cl$, 61 °C/20 mmHg (lit.[14] 52 °C/10 mmHg). $EtOSO_2F$ and $EtOSO_2CF_3$ were obtained in the same manner as reported.[2] $MeOSO_2F$ was prepared by the reaction of dimethyl sulfate with FSO_3H,[2] bp 92—94 °C. THP was dried on sodium metal and distilled. This procedure was repeated twice. Purification of CH_2Cl_2 was carried out in the same way as in the previous work.[2] Nitrobenzene was dried on phosphorus pentoxide and distilled *in vacuo*.[7] Chlorobenzene and $CHCl_3$ (an internal standard) were dried on Molecular Seives and distilled before use. Liquid SO_2 was obtained by condensation of gaseous SO_2 (Seitetsu Kagaku Co., Ltd).

Kinetic Procedures. Kinetic reactions were carried out under nitrogen. A typical run is as follows. Into an NMR sample tube containing 0.752 ml of CH_2Cl_2, 0.088 ml (0.822 mmol) of $EtOSO_2Cl$, 0.081 ml (0.835 mmol) of THP, and 0.080 ml (1.00 mmol) of $CHCl_3$ were introduced with a microsyringe, giving the initial concentrations of $[E]_0=0.822$ mol/l and $[T]_0=0.835$ mol/l. During the sample preparation the NMR sample tube was cooled in a Dry Ice–acetone bath. The tube was sealed, and inserted into the probe of the NMR spectrometer (Hitachi R-20B). Up to this step the extent of the reaction was negligible. The reaction was then followed by taking spectra several time at the desired temperature. For the determination of equilibrium concentration, the sample tube was kept at the same temperature until the reaction no longer proceeded. The NMR spectrum was then recorded. The oxonium concentration of the spectrum was taken to be an $[Ox]_e$ value. The reaction temperature was kept constant within ±1 °C and the experimental error of the integration was within ±2%.

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