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OXYGEN ENHANCEMENT OF THE ELECTRON CAPTURE DETECTOR RESPONSE OF CARBON DIOXIDE

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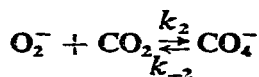
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SUMMARY

Simmonds has reported that the response of the electron capture detector to carbon dioxide is markedly enhanced by the addition of oxygen. The kinetic model of the electron capture detector has been modified by including the reaction



as well as the usual oxygen attachment and detachment reactions. This leads to an expression for the response which agrees well with the concentration dependency and the unique temperature variation; increasing at low temperatures, reaching a maximum at 500°K and decreasing at high temperatures. From this expression, activation energies of $E_2^* = 0.95 \pm 0.2$ eV and $E_{-2}^* = 2.16 \pm 0.2$ eV are obtained.

INTRODUCTION

The electron capture detector (ECD) has long been recognized as a valuable sensitive and selective detector. Recently, oxygen has been added to the carrier gas to modify the selectivity by means of ion molecule reactions of the oxygen negative ion. Grimsrud and co-workers¹⁻³ worked primarily with halogenated compounds while Simmonds⁴ reported the effect with carbon dioxide. In the case of the halogenated compounds, the constant-current mode was used and a steady-state kinetic model was devised by assuming that the pulse frequency is proportional to the electron concentration³. Simmonds⁴ used the constant-frequency mode which has been studied more extensively from a theoretical basis, but he did not present a kinetic model for

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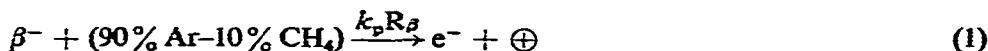
the reactions. Instead, a number of possible reactions were presented to explain the phenomenon. On the basis of previous studies of thermal energy processes in mixtures containing carbon dioxide and oxygen using drift tubes^{5,6}, flowing afterflows^{7,8} and mass spectrometric methods⁹⁻¹², the enhancement reaction is clearly:



This is a specific case where a second negative ion, if formed, is in equilibrium with the O_2^- . It is the purpose of this paper to extend the kinetic model of the ECD originally presented by Wentworth *et al.*¹³ to this type of enhancement reaction and to apply results of this model to the data presented by Simmonds⁴ for the case of carbon dioxide. The details of the exact derivation will be presented in a future paper along with data for other reactions of this nature.

REACTION SCHEME FOR THE OXYGEN ENHANCEMENT VIA THE FORMATION OF A NON-DISSOCIATIVE NEGATIVE ION

The reactions taking place in the ECD in the presence of oxygen are:



In the presence of a species, AB, which can react associatively with O_2^- we have the reaction:



and the neutralization of the new negative ion:



In general, the new negative ion can be formed by the three body reaction:



or can be formed by the reaction of AB^- with oxygen:



In the specific case of carbon dioxide, the direct electron attachment is very small so that the latter reaction sequence is negligible. The three body reaction is not obviously negligible but in fact, the temperature dependency demonstrates that reaction 7 is much less probable than reaction 5.

The reactions 1-6 lead to a series of second order differential equations which should be solved by an exact iterative procedure as given recently by Wentworth and Chen¹⁴. However, if the fraction of the electrons removed by the reaction with carbon dioxide and/or oxygen is low, *i.e.* 10-20%, then the second order equations approach first order equations as a limit and the steady state results can be obtained simply as given in previous references^{13,15}. The first order rate constants are designated as $k_D = k'_D [\oplus]$; $k_{L1} = k'_{L1} [\oplus]$ and $k_{L2} = k'_{L2} [\oplus]$. Also, the concentrations of oxygen and carbon dioxide are assumed constant and are designated as a and c respectively. Then assuming steady state for the concentrations of O₂⁻, CO₂⁻ and e⁻, we derive expressions for the electron concentration with no capturing species, designated b , the electron concentration in the presence of oxygen, designated [e⁻]_{O₂}, and the electron concentration in the presence of oxygen and carbon dioxide, designated [e⁻]_{CO₂,O₂}. These can be combined to give the relationship between the enhanced response and the various rate constants.

$$\Delta \frac{b - e}{c} = \left(\frac{b - [e^-]_{CO_2, O_2}}{[e^-]_{CO_2, O_2}} - \frac{b - [e^-]_{O_2}}{[e^-]_{O_2}} \right) \quad (10)$$

$$\Delta \frac{b - e}{c} = \frac{\left(\frac{k_1 a}{k_D} \right) \left(\frac{k_{L2}}{k_{L1}} \right) \left(\frac{k_2 c}{(k_{-2} + k_{L2})} \right) \left(\frac{k_{-1}}{k_{L1}} \right)}{\left(1 + \frac{k_{-1}}{k_{L1}} \right) \left(1 + \frac{k_{-1}}{k_{L1}} + \frac{k_{L2}}{k_{L1}} \left(\frac{k_2 c}{(k_{-2} + k_{L2})} \right) \right)} \quad (11)$$

This gives the response as a function of five ratios of rate constants, two of which are characteristic of oxygen, and three of which are characteristic of the enhancement reactions. The rate constant ratios can be expressed as a pre-exponential term times an exponential term, *i.e.* $k = A(T)\exp(E/kT)$. Eqn. 11 then forms the basis of the comparison of the experimental data with the kinetic model for low capture.

RESULTS

The thermal electron capture data for oxygen have been reported by Van de Wiel and Tommassen¹⁶ and by Freeman¹⁷. The former obtained an electron affinity of 0.43 ± 0.05 eV and an activation energy for attachment of 0.07 ± 0.05 eV. The data obtained by Freeman are shown in Fig. 1 where $\ln KT^{3/2}$ is plotted *versus* 1/T. The slope in the high temperature region is proportional to the electron affinity while the slope in the low temperature region is proportional to the activation energy for the forward reaction^{13,17}. The line drawn through the data is the least squares line calculated from the parameters given above.

The oxygen enhanced ECD response reported by Simmonds⁴ for carbon dioxide and nitrous oxide have been converted to electron capture coefficients, K ,

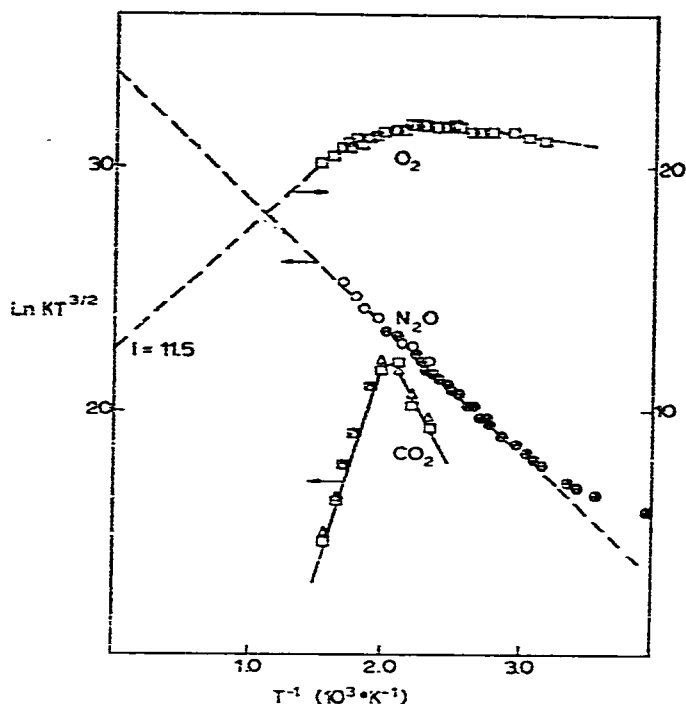


Fig. 1. $\ln KT^{3/2}$ versus $1/T$ for oxygen (\square) (ref. 17, y -axis displaced); nitrous oxide (\ominus) (ref. 18); nitrous oxide in oxygen-doped nitrogen (\circ); and carbon dioxide in oxygen-doped-nitrogen (Δ , calculated; \square , experimental).

and are shown in Fig. 1 as $\ln KT^{3/2}$ vs. $1/T$. The reliability of the temperature dependency data obtained by Simmonds is indicated by the fact that his nitrous oxide data blends continuously into earlier data obtained in the normal ECD mode by Wentworth and co-workers^{13,19} which are also shown in Fig. 1.

The enhanced response can be calculated as a function of temperature by using various values of the pre-exponential and exponential terms for the rate constants in eqn. 11. This has been done on a TI-58 programmable calculator and the results are shown in Fig. 1 where the agreement is obvious. The parameters used in this calculation are given in Table I. This set is probably not unique but does represent a reasonable set based upon previous data as will be discussed in the next section. These parameters were also used to calculate the concentration dependency of the enhanced response and the agreement obtained was good.

TABLE I

RATE CONSTANT RATIOS USED IN THE CALCULATION OF THE ENHANCED RESPONSE

$k_{12}/k_{11} = 3$
$k_{12}/k_D = 2.640 \exp(-0.070/kT)$
$k_{-1}/k_{11} = 30.936 T^{3/2} \exp(-0.510/kT)$
$k_2/k_{11} = 22.619 \cdot 10^9 \exp(-0.95/kT)$
$k_{-2}/k_{11} = 63.720 \cdot 10^{10} T^{3/2} \exp(-2.16/kT)$

DISCUSSION

The first step in examining the ECD results is to consider the response to oxygen alone. The electron affinity has been determined experimentally by several techniques with the "best" value being the photodetachment result of 0.440 ± 0.007 eV (ref. 20). The first accurate experimental determination of this quantity (0.43 eV) was by Packs and Phelps^{5,6} who studied the temperature dependency of the attachment and detachment processes. This is essentially the same type of determination as carried out in the ECD and the agreement between the ECD values of 0.5 eV and 0.43 eV and the above "best" value is good^{16,17}. The most extensive data for the activation energy of the attachment process comes from the ECD results given by Freeman¹⁷. This value of 0.07 eV is a rather low value and is qualitatively in agreement with the zero activation energy reported by Packs and Phelps⁵ and Van de Wiel and Tommasen¹⁶.

The parameters for the enhancement reactions are not as well established as those for oxygen alone. The ratio of the recombination rate constants, k_{L2}/k_{L1} , for the negative ions CO₄⁻ and O₂⁻ respectively, should be in the range 0.1 to 10 and should be relatively independent of temperature. In the calculations, this parameter was varied over this range and for the particular activation energies obtained in the next section, a value of three ultimately gave the best fit to the experimental data.

Several estimates of the thermochemical stability of CO₄⁻ relative to O₂⁻ and carbon dioxide ΔE_2 have been made and are listed in Table II. Packs and Phelps⁶ also obtained estimates of the rate constants k_2 and k_{-2} at a single temperature, 450°K. The only estimate of the activation energies E_2^* and E_{-2}^* comes from an indirect calculation. Pacansky *et al.*²¹ estimated that the energy required to bend carbon dioxide in the formation of CO₂⁻ is 0.76 eV (Table II). If it is then assumed that the formation of CO₄⁻ requires a similar bending, then E_2^* would be about the same.

TABLE II

ENERGETICS AND ACTIVATION ENERGIES FOR THE REACTION O₂⁻ + CO₂ = CO₄⁻

E_2^* (eV)	E_{-2}^* (eV)	ΔE_2 (eV)	Method	References
$0.9_5 \pm 0.1$	$2.1_6 \pm 0.1$	-1.2 ± 0.2	ECD temperature dependence	This work
0.76			Calculations	Pacansky <i>et al.</i> ²¹
		-0.80 ± 0.1	Drift tube temperature dependence	Packs and Phelps ^{5,6}
		-0.8	Flowing afterglow	Adams <i>et al.</i> ¹⁰
		-1.1 ± 0.2	Photodetachment	Vestal and Mauclaire ¹¹

Thus these parameters were taken as starting points to try to fit the experimental enhancement data to eqn. 11. However, the dramatic temperature dependency could not be reproduced. Therefore, the magnitudes of the rate constants at 460°K were held constant and the energies varied until a good fit was obtained. The final results are given in Table II. The ECD results for ΔE_2 agree well with the photodetachment results. The agreement with the other values is not bad and could even be within the experimental error.

In order to appreciate the way that these parameters affect the temperature dependency of the enhanced response better, the low and high temperature limits of eqn. 11 will be examined. At low temperatures, the reverse reaction rate constants become small and the recombination rate constants predominate, *i.e.* $k_{L2} > k_{-2}$ and $k_{L1} > k_{-1}$ so that eqn. 11 becomes:

$$\Delta \frac{b - c}{c} = \frac{k_1 k_2 k_{-1}}{k_D k_{L1} k_{L2}} ac \quad (12)$$

Thus the steep positive slope in the low temperature region is due to the product $k_1 k_2 k_{-1}$ or the sum of the activation energies $E_1^* + E_2^* + E_{-1}^*$. At high temperatures, the reverse reaction rate constants predominate over the recombination rate constants, *i.e.* $k_{-2} > k_{L2}$ and $k_{-1} > k_{L1}$ so that eqn. 11 becomes

$$\Delta \frac{b - c}{c} = \frac{k_{L2} k_1 k_2}{k_D k_{-1} k_{-2}} ac \quad (13)$$

The steep negative slope in the high temperature region is due to the product $(k_1/k_{-1})(k_2/k_{-2})$ or the sum of the activation energies, $E_1^* + E_2^* - E_{-1}^* - E_{-2}^*$. The sharp maximum is due to the transition from one region to the other occurring over a narrow temperature range.

CONCLUSIONS

(1) The enhancement of the ECD by oxygen doping in the case of carbon dioxide is due to the formation of CO_4^- by the reaction of O_2^- and CO_2 .

(2) The kinetic model of the electron capture processes can be modified to include the above reaction and the recombination of CO_4^- and leads to an expression for the enhanced response which agrees with the temperature and concentration variations of the experimental results.

(3) The value of ΔE_2 obtained from the ECD data, -1.2 ± 0.2 eV, agrees with the photo-detachment result¹¹ and is only slightly higher than the drift tube^{5,6} and the flowing afterglow^{9,10} results.

(4) The value of E_2^* , 0.95 ± 0.1 eV is consistent with the calculated value of the energy required to bend carbon dioxide prior to electron attachment²¹.

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