Electron Spin Resonance Study of the Kinetics of the Reaction of Oxygen($^1\Delta_g$) with Tetramethylethylene and 2,5-Dimethylfuran[1]

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Abstract: In this paper we report the first quantitative measure of the temperature dependence of gas-phase reactions of $O_2(^1\Delta_g)$. The reactions of $O_2(^1\Delta_g)$ with tetramethylethylene and 2,5-dimethylfuran were investigated over the temperature range of 298–460°K. The Arrhenius-type rate constants obtained for these two reactions were $(7.15 \pm 0.88) \times 10^{11} \exp(-3500 \pm 100/RT)$ and $(7.24 \pm 0.70) \times 10^{10} \exp(-1070 \pm 60/RT)$ cm^3 mol^{-1} sec^{-1}, respectively. Using the esr method, combined with results from other workers, it is possible to show that the chemical reaction of these molecules with $O_2(^1\Delta_g)$ is much faster than any collisional deactivation process. It was also possible to show that low molecular weight straight-chain olefins, such as ethylene and propylene, must react at least two orders of magnitude slower than the tetramethylethylene molecule at 298°K. The results obtained in the present study are in good agreement with the recent mass spectrometric study of Herron and Huie of these reactions at 300°K.

The reactions of $O_2(^1\Delta_g)$ with various molecules have received considerable attention in recent years. The interest in these reactions have been stimulated by the suggestion that $O_2(^1\Delta_g)$ molecules might play an active role in photochemical air pollution. However, despite the numerous investigations of $O_2(^1\Delta_g)$ reactions, there are relatively few quantitative data available on the absolute rate constants of these reactions, and no data have been obtained on the temperature dependence of these reactions in the gas phase. Furthermore, it is of interest to note that the two recent papers reporting on the chemical reactivity of $O_2(^1\Delta_g)$ are not in agreement. Herron and Huie[2] obtained a rate constant for the reaction of $O_2(^1\Delta_g)$ with olefins which is several orders of magnitude lower than that discussed by Kummler, *et al.*[3]

We wish to report here on the investigation of the kinetics of the reactions of $O_2(^1\Delta_g)$ using esr spectroscopy to monitor the $O_2(^1\Delta_g)$ concentration. The esr absorption spectra of $O_2(^1\Delta_g)$ were first observed and discussed by Falick, *et al.*[4] We have used one of the four lines of the $\Delta m_J = 1$ transitions of the $J = 2$ state to follow the rate of removal of the $O_2(^1\Delta_g)$. Using this method we were able to measure, with good precision, the rate of $O_2(^1\Delta_g)$ reaction with tetramethylethylene (TME) and 2,5-dimethylfuran (DMF) over the temperature range of 298–460°K. From these data, we are able to evaluate the separate Arrhenius parameters for these two reactions.

Experimental Section

The flow apparatus employed was similar to that developed by Westenberg and deHaas,[5a] and it has been described elsewhere.[5b] Excited oxygen molecules were produced by the electrodeless discharge of O_2. In some experiments the O_2 was diluted with added helium. The O atoms produced in the discharge were removed by passing the discharged gas over a film of HgO.[6] The removal of these O atoms could be followed by the elimination of their esr absorption signals.

The usual procedure of taking "on" and "off" readings of the $O_2(^1\Delta_g)$ concentration with the stable reactant flowing through the injector followed by readings with the reactant in the bypass position were carried out to compensate for wall loss of excited O_2. In general, this correction became significant only at temperatures above 100° and wall loss increased slowly with increasing temperature. As the temperature increased above 100°, a decreasing $O_2(^1\Delta_g)$ esr signal was obtained for a given flow of O_2. In addition, the $O_2(^1\Delta_g)$ signal would increase markedly with the removal of the injector from the reaction furnace at these higher temperatures. The decrease in esr signal at the higher temperatures limited our temperature studies to a high-temperature limit of 460°K.

The rate constant for the reaction

$$O_2(^1\Delta_g) + B \longrightarrow \text{products}$$

where B is the stable reactant gas, is evaluated from the equation

$$\ln([O_2(^1\Delta_g)]_{B=0}/[O_2(^1\Delta_g)]) = k[B]t \qquad \text{(I)}$$

The left-hand side represents the ratio of the esr signal intensities in the absence and presence of B for a given injector position. The time, t, is simply the distance of the injector from some arbitrary zero position divided by the flow velocity. Since all quantities in eq I are known, or easily measured, the specific rate constant, k, can be calculated.

The derivation of eq I and the assumptions involved have been discussed by Westenberg.[7] The only assumption which need be questioned with respect to the present study is the one which assumes negligible change in the concentration of the stable reactant during the course of a given run. This is usually accomplished by simply making the partial pressure of stable reactant much larger than the pressure of the discharged molecule which produces the atomic or radical species. However, in the present work it was necessary to discharge rather high pressures of oxygen in order to obtain measurable amounts of $O_2(^1\Delta_g)$. Thus, as shown in Tables I and II, the flow conditions employed were such that the concentration of stable reactant was less than that of the oxygen entering the discharge. However, it has been established that only a small fraction of the O_2 is actually converted to $O_2(^1\Delta_g)$ in the discharge.[8] This was confirmed in the current experiments in that a decrease of the ground state O_2 signal of only 6–10% was observed upon the initiation of the discharge. Since a large fraction of this decrease leads to O atom production, one can place an upper limit of only a few per cent $O_2(^1\Delta_g)$ formed relative to the metered flow of oxygen. This fact was confirmed by noting that changes in the ratio of TME to O_2 by a factor of 3.5 had no observable effect on

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(1) The authors are pleased to acknowledge the financial support of the National Air Pollution Control Administration for support of this work under Research Grant No. AP00502.

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Table I. Experimental Results Used to Evaluate the Rate Constant for the Reaction $O_2(^1\Delta_g)$ + Tetramethylethylene

T, °K	P, Torr	V, cm/sec	[TME], mol/cm³	[TME]/[O₂]	k, cm³/(mol sec)
298	0.40	342	2.35×10^{-9}	0.12	2.07×10^{9}
	0.44	344	4.58×10^{-9}	0.24	2.05×10^{9}
	0.47	315	3.62×10^{-9}	0.17	1.75×10^{9}
	0.49	586	1.74×10^{-9}	0.23	1.90×10^{9}
	0.53	329	6.96×10^{-9}	0.32	1.60×10^{9}
	0.54	563	3.40×10^{-9}	0.43	1.50×10^{9}
					$k = (1.81 \pm 0.20) \times 10^{9}$
351	0.42	815	1.86×10^{-9}	0.35	5.52×10^{9}
	0.43	776	1.32×10^{-9}	0.23	5.65×10^{9}
	0.53	603	1.62×10^{-9}	0.23	5.67×10^{9}
	0.55	640	2.37×10^{-9}	0.32	3.07×10^{9}
					$k = (4.98 \pm 0.95) \times 10^{9}$
396	0.44	869	8.18×10^{-10}	0.15	1.02×10^{10}
	0.45	863	1.14×10^{-9}	0.20	9.87×10^{9}
	0.47	880	2.25×10^{-9}	0.41	7.41×10^{9}
	0.55	876	2.16×10^{-9}	0.25	8.51×10^{9}
					$k = (9.00 \pm 1.04) \times 10^{9}$
454	0.42	1120	3.58×10^{-10}	0.07	1.63×10^{10}
	0.44	1115	8.88×10^{-10}	0.16	9.33×10^{9}
	0.44	1149	1.08×10^{-9}	0.19	1.81×10^{10}
	0.47	1083	1.51×10^{-9}	0.26	9.00×10^{9}
					$k = (1.32 \pm 0.40) \times 10^{10}$

Table II. Experimental Results Used to Evaluate the Rate Constant for the Reaction $O_2(^1\Delta_g)$ + 2,5-Dimethylfuran

T, °K	P, Torr	V, cm/sec	[DMF], mol/cm³	[DMF]/[O₂]	k, cm³/(mol sec)
298	0.38	680	7.47×10^{-10}	0.16	1.18×10^{10}
	0.41	666	5.61×10^{-10}	0.09	1.06×10^{10}
	0.42	674	9.50×10^{-10}	0.15	1.30×10^{10}
	0.43	694	1.15×10^{-9}	0.16	9.82×10^{9}
	0.50	608	1.67×10^{-9}	0.21	9.84×10^{9}
					$k = (1.10 \pm 0.11) \times 10^{10}$
330	0.40	688	5.43×10^{-10}	0.10	1.39×10^{10}
	0.42	758	7.05×10^{-10}	0.14	1.55×10^{10}
	0.44	788	4.74×10^{-10}	0.10	1.84×10^{10}
	0.46	808	7.93×10^{-10}	0.14	1.57×10^{10}
					$k = (1.59 \pm 0.13) \times 10^{10}$
356	0.30	682	6.65×10^{-10}	0.12	1.81×10^{10}
	0.41	858	3.94×10^{-10}	0.08	1.19×10^{10}
	0.42	810	5.60×10^{-10}	0.12	1.54×10^{10}
	0.43	806	7.62×10^{-10}	0.15	1.47×10^{10}
	0.43	840	8.58×10^{-10}	0.16	2.14×10^{10}
					$k = (1.63 \pm 0.27) \times 10^{10}$
393	0.31	778	4.13×10^{-10}	0.11	1.74×10^{10}
	0.46	878	3.96×10^{-10}	0.08	1.64×10^{10}
	0.49	836	7.03×10^{-10}	0.14	1.93×10^{10}
	0.50	931	7.74×10^{-10}	0.11	1.82×10^{10}
					$k = (1.78 \pm 0.10) \times 10^{10}$
459	0.26	972	2.75×10^{-10}	0.07	2.84×10^{10}
	0.37	970	2.75×10^{-10}	0.07	2.25×10^{10}
	0.42	1065	2.51×10^{-10}	0.07	1.42×10^{10}
	0.42	1082	4.69×10^{-10}	0.13	2.55×10^{10}
	0.45	1042	5.89×10^{-10}	0.14	1.91×10^{10}
					$k = (2.19 \pm 0.43) \times 10^{10}$

the measured rate constant (Table I). Furthermore the $O_2(^1\Delta_g)$ decay plots, as shown in Figure 1, were linear over a range of 2.5-fold change in the concentration of $O_2(^1\Delta_g)$. If significant quantities of the TME or DMF are consumed in a given run, these plots would shown downward curvature. Linear plots were obtained in all runs used in the evaluation of the reaction rate constants. However, it was noted that in runs where the ratio TME:O_2 was less than 0.07, some downward curvature was obtained.

Actually it is possible, using the procedure developed by Westenberg and deHaas,[9] to determine quantitatively the concentration of $O_2(^1\Delta_g)$. In this particular case, the $O_2(^1\Delta_g)$ concentration is computed relative to a known concentration of $O_2(^3\Sigma_g)$. The details of the procedure as well as the various equations involved are given in ref 9. It will suffice to say that, in the present case, the application of this method reduces to the following equation.

$$\frac{N_{O_2(^1\Delta_g)}}{N_{O_2(^3\Sigma_g)}} = \frac{\left[g_{\text{eff}} Z e^{E_i/kT} |(\mu_r)_{ij}|^2 \int_0^\infty \chi_{ij}''\,\mathrm{d}H\right]_{O_2(^1\Delta_g)}}{\left[g_{\text{eff}} Z e^{E_i/kT} |(\mu_r)_{ij}|^2 \int_0^\infty \chi_{ij}''\,\mathrm{d}H\right]_{O_2(^3\Sigma_g)}} \qquad \text{(II)}$$

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(9) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, 40, 3087 (1964).

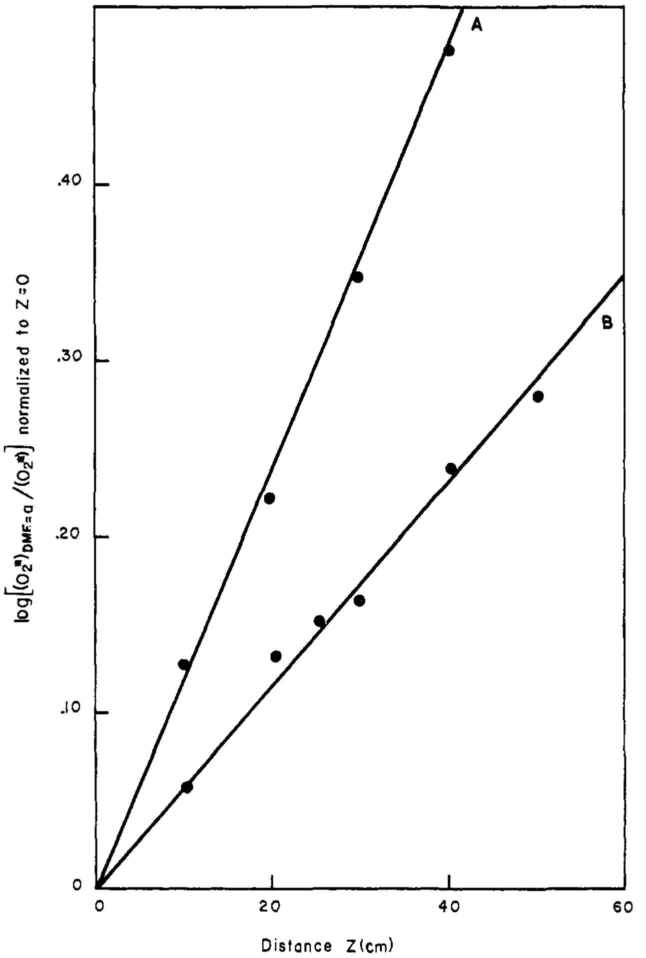


Figure 1. Typical examples of $O_2(^1\Delta_g)$ decay plots in runs with DMF: curve A, pressure = 0.5 Torr, velocity = 608 cm/sec, [DMF] = 1.67×10^{-9} mol/cm³, T = 298°K; curve B, pressure = 0.38 Torr, velocity = 680 cm/sec, [DMF] = 7.47×10^{-10} mol/cm³, T = 298°K.

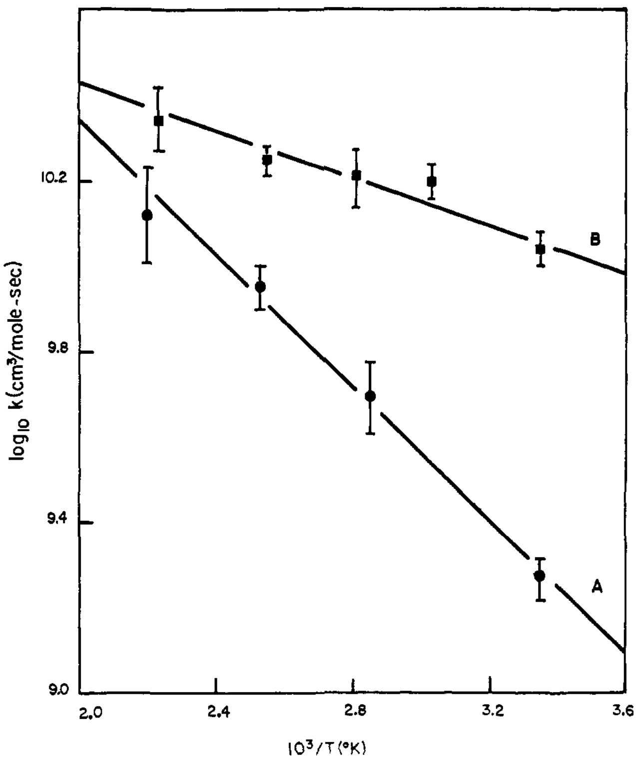
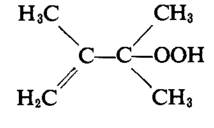


Figure 2. Arrhenius plot of the results obtained in the reactions of $O_2(^1\Delta_g)$ with TME (curve A) and with DMF (curve B).

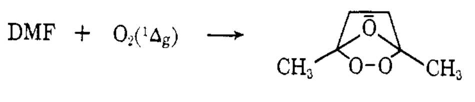
In this equation Z is the partition function for the absorbing species, E_i is the energy of the lower state involved in the transition, $|(\mu_r)_{ij}|^2$ is the square of the absolute value of the transition matrix element in the direction of the microwave magnetic field, the $\int_0^\infty \chi_{ij}''\mathrm{d}H$ represents the integration of the whole absorption line for the imaginary part of the magnetic susceptibility, where H is the magnetic field strength. For molecules such as $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g)$ the value of g_{eff} is dependent upon which line of the spectrum is employed. In our case we have used the lowest line of the $J = 2$ transitions of $O_2(^1\Delta_g)$ and the E line[9] of $O_2(^3\Sigma_g)$, having values of g_{eff} of 0.67 and 1.24, respectively. The ratio of partition functions for $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g)$ reduces to a factor of 2/3. The E line of the $O_2(^3\Sigma_g)$ molecule was chosen for the reference signal as the value of $|(\mu_r)_{ij}|^2$ for this line is essentially the same as that for the lowest line of $O_2(^1\Delta_g)$ and thus these terms cancel. The integration of the magnetic susceptibility over the magnetic field was carried out using the fact that the first moment of the signal is proportional to the true integrated intensity, independent of modulation amplitude or modulation frequency.[10] The first moments were obtained by numerical integration of the recorded signal. Substitution of the various ratios into eq II above gave $N_{O_2(^1\Delta_g)}/N_{O_2(^3\Sigma_g)} = 0.05$ for the case of a discharge in pure oxygen. Thus, we conclude that under our operating conditions 5% of the oxygen entering the discharge is converted to $O_2(^1\Delta_g)$.

Results and Discussion

The results obtained in the TME + $O_2(^1\Delta_g)$ reactions are shown in Table I. Treatment of these data by the method of least squares leads to a rate constant of $(7.15 \pm 0.88) \times 10^{11} \exp[(-3500 \pm 100)/RT]$ cm³ mol⁻¹ sec⁻¹ for this reaction. From the work of other workers on this and related reactions, it is apparent that this reaction leads to the formation of the peroxide[11]



The corresponding data in the DMF reactions are given in Table II. Analysis of these data, again by least squares, results in a rate constant of $(7.24 \pm 0.70) \times 10^{10} \exp[(-1070 \pm 60)/RT]$ cm³ mol⁻¹ sec⁻¹ for the reaction



It is of interest to compare these results with those obtained by Herron and Huie[2] for the same reactions. At 300°K they obtained values of $(1.0 \pm 0.3) \times 10^9$ and $(1.6 \pm 0.4) \times 10^{10}$ cm³ mol⁻¹ sec⁻¹ for the $O_2(^1\Delta_g)$ reactions with TME and DMF, respectively. These values are in good agreement with those obtained in the present work, $(1.81 \pm 0.20) \times 10^9$ and $(1.10 \pm 0.11) \times 10^{10}$, respectively. What is particularly significant in this comparison is that the experiments of Herron and Huie were carried out under very different flow conditions. Furthermore, these reactions were followed by mass spectrometric analysis of the decrease in the partial pressure of the stable reactants and by the increase in the partial pressure of the product adduct. The good agreement between the two separate in-

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(10) K. Halbach, *Phys. Rev.*, **119**, 1230 (1960).

(11) See, for example, K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

vestigations confirms that the stoichiometry of one molecule of $O_2(^1\Delta_g)$ consumed per molecule of stable reactant must be correct. Whereas our TME results are somewhat higher than theirs, our DMF results are lower. If the stoichiometry of these reactions was not a one to one ratio, then the two sets of results would be systematically different. In addition, since we followed the reaction by the rate of $O_2(^1\Delta_g)$ removal, it shows that collisional deactivation of the excited O_2 by TME or DMF is negligibly slow compared to the chemical reactions.

A comparison of the temperature dependence of these two reactions is shown in Figure 2. The higher preexponential factor of the TME reaction compared to the DMF reaction will lead to an ultimate inversion of reactivity at sufficiently high temperatures. It is of interest to note that the lower preexponential factor observed in the DMF reaction is consistent with expectations based on entropy changes in forming the activated complex. The formation of a cyclo addition product in this reaction would be expected to lead to an unusually large entropy decrease. From the thermodynamic formulation of reaction rates it is easy to show that for a bimolecular reaction the Arrhenius preexponential factor can be equated to the term (ekT/h) $\exp(\Delta S_c^{\ddagger}/R)$, where $\Delta S_c^{\ddagger}$ is the entropy change, in units of molarity, in going from reactants to activated complex. Thus the observation of the much lower preexponential factor obtained in the DMF reaction implies that the cyclization is essentially complete in the activated complex.

We also investigated a number of reactions of $O_2(^1\Delta_g)$ with various straight-chain olefins. In each case the reaction was too slow to be measured using the esr method. From a knowledge of flow velocities employed in experiments with propylene we calculate that the $O_2(^1\Delta_g)$ + propylene reaction must be slower than 5×10^7 cm^3 mol^{-1} sec^{-1} at 298°K. These results confirm the findings of Herron and Huie.[2] Actually in these experiments we observed no measurable decrease in the $O_2(^1\Delta_g)$ concentration. This again demonstrates that collisional deactivation of $O_2(^1\Delta_g)$ by low molecular weight olefins must be a relatively slow process.

X-Ray Photoelectron Spectroscopy of Halomethanes[1a]

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Abstract: Carbon 1s ionization potentials, relative to that of methane (290.8 eV), have been measured for CH_3F (2.8 eV), CHF_3 (8.3 eV), CF_4 (11.0 eV), CH_3Cl (1.6 eV), CH_2Cl_2 (3.1 eV), $CHCl_3$ (4.3 eV), CCl_4 (5.5 eV), and CH_3Br (1.0 eV), together with fluorine 1s ionization potentials for CH_3F (692.4 eV), CHF_3 (694.1 eV), and CF_4 (695.0 eV), and chlorine 2s ionization potentials for CH_3Cl (277.2 eV), CH_2Cl_2 (277.6 eV), $CHCl_3$ (277.7 eV), and CCl_4 (278.0 eV). The carbon and halogen binding energies increase linearly with the number of halogens. Comparison of the fluorocarbon results with binding energies based on use of Koopmans' theorem indicates that there is a substantial absolute error between experiment and theory, but that the Koopmans'-theorem results account fairly well for the relative ionization potentials in this series of compounds. The measured binding energies are found to vary linearly with the sum of differences between the electronegativities of the ligands and that of hydrogen. A plausible reason is developed for this linear relationship.

Inner-electron binding energies for extensive series of nitrogen, sulfur, and chlorine compounds have been determined by X-ray photoelectron spectroscopy.[2-4] These and other measurements show that the binding energies of the inner electrons increase with oxidation number, with formal charge on the atom, and with increasing electronegativity of the ligands attached to the atom. Some success has been obtained in correlating the measured shifts with charges assigned to atoms in various ways. The technique shows some promise of providing information on charge distributions in molecules and quantitative information on the electronegativity of different ligands.

Some information has been published on the carbon 1s electron binding energies in different compounds and the results are generally in agreement with expectations.[5,6] However, no systematic study of carbon compounds has yet appeared. As part of such a study, we report here the carbon 1s binding energies for the compounds CH_4, CH_3F, CHF_3, CF_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, and CH_3Br. In addition, we report the fluorine 1s and chlorine 2s binding energies. These compounds provide a series in which the electro-

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(2) (a) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindbreg, "ESCA Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksell, Uppsala, 1967, pp 97–137; (b) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1967).

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(6) Reference 2a, pp 78–79, 137–3.