Kinetics of Ring Opening of Substituted Cyclobutenediones by Platinum(0) Complexes

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Kinetic data are reported for ring opening of benzocyclobutene-1,2-dione, 3-phenylcyclobutene-1,2-dione, 4-methoxy-3-phenylcyclobutene-1,2-dione, and 3,4-dimethoxycyclobutene-1,2-dione with the zerovalent platinum complexes $[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2]$ and $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$. Possible mechanisms, intramolecular in chloroform and dissociative in benzene, are proposed in the light of these results.

THE reaction of benzocyclobutene-1,2-dione, (I), with platinum(0) complexes results in unsymmetrical cleavage of the cyclobutene ring to give platinum(II) compounds, (II).[1] Reactions of substituted cyclobutene-1,2-diones, (IIIa—IIIc), with platinum(0) complexes also lead to analogous platinacyclopentene compounds, (IV). In the case of compound (IIIa) an intermediate alkene complex (Va) has been characterised. The reaction of compound (IIId) with platinum(0) complexes yields only the alkene complex (Vb); further reaction to a platinacyclopentene derivative has not been observed.[2]

In the present paper we report the kinetics of reaction of (I) with several platinum(0) complexes to give (II), (IIIb) and (IIIc) to give compounds (IVb) and (IVc), and the rearrangement of complex (Va) which gives (IVa). Mechanisms for the reactions of (I) to (II) and (Va) to

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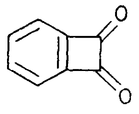
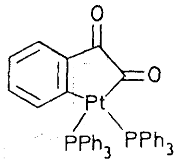
[1] J. A. Evans G. F. Everitt, R. D. W. Kemmitt, and D. R. Russell, *J.C.S. Chem. Comm.*, 1973, 158.

[2] E. R. Hamner, R. D. W. Kemmitt, and M. A. R. Smith, *J.C.S. Chem. Comm.*, 1974, 841.

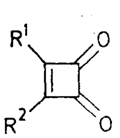
(IVa) are proposed on the basis of the kinetic results, and mechanisms for (IIIb) to (IVb) and (IIIc) to (IVc) are discussed in similar terms.



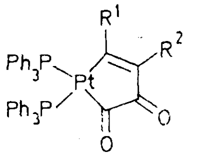
(I)



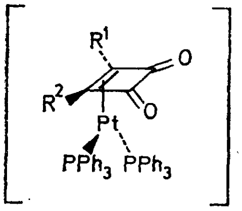
(II)



(IIIa) R^1 = Ph, R^2 = H
(IIIb) R^1 = Ph, R^2 = OMe
(IIIc) R^1 = R^2 = OMe
(IIId) R^1 = Ph, R^2 = Me



(IVa) R^1 = Ph, R^2 = H
(IVb) R^1 = Ph, R^2 = OMe
(IVc) R^1 = R^2 = OMe



(Va) R^1 = Ph, R^2 = H
(Vb) R^1 = Ph, R^2 = Me

RESULTS AND DISCUSSION

Reaction of Benzocyclobutene-1,2-*dione*.—Benzocyclobutene-1,2-dione, (I), reacted quantitatively with tetrakis(triphenylphosphine)platinum(0), $[Pt(PPh_3)_4]$, with (η-*trans*-stilbene)bis(triphenylphosphine)platinum(0), $[Pt(PhCH{=}CHPh)(PPh_3)_2]$, and with ($\eta$-diphenylacetylene)bis(triphenylphosphine)platinum(0), $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$, to give the platinacyclopentenedione compound (II). In benzene solution at room temperature the reaction with the stilbene complex was complete within a few seconds, the reaction with the tetrakis(phosphine) complex had a half-life of only *ca.* 50 s, and the reaction with the diphenylacetylene complex had a half-life greater than 1 000 s. We therefore studied the kinetics of the last-named reaction.

In mixtures containing an excess of (I), the reaction was first order in the concentration of the platinum(0) complex. Observed first-order rate constants are reported in Table 1. It is clear that the order of the reaction with respect to the dione concentration is zero. Thus the rate-determining step must be loss of diphenylacetylene from the complex. This assignment is consistent with the faster reactions observed for the dione with $[Pt(PPh_3)_4]$ and with $[Pt(PhCH{=}CHPh)(PPh_3)_2]$, as one would expect the loss of PPh_3 or of stilbene from these complexes to be faster than that of diphenylacetylene from $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$.[3] From the kinetic results in Table 1 the activation parameters for loss of diphenylacetylene were computed as $\Delta H^{\ddagger} = 118 \pm 4$ kJ mol^{-1} and $\Delta S^{\ddagger} = +85 \pm 13$ J K^{-1} mol^{-1}.* The positive value for the activation entropy is consistent with dissociative loss of diphenylacetylene in the rate-determining step.

TABLE 1

Observed first-order rate constants ($10^4k_{obs.}/s^{-1}$) for the reaction of benzocyclobutene-1,2-dione with $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ (2.0×10^{-3} mol dm^{-3}) in benzene solution

	10^2[dione]/mol dm^{-3}					
T/K	1.0	2.0	3.0	4.0	5.0	6.0
291.2	1.6	1.4	1.5	1.3		1.5
299.6	4.6	4.6	4.8	4.8	4.8	4.6
307.2		15.2	15.9	14.6	15.0	15.5
316.2	75		77	76		75

The observed kinetic pattern for this reaction implies that insertion of the platinum into the cyclobutene ring is a relatively rapid step subsequent to the rate-determining generation of a transient, reactive, $[Pt(PPh_3)_2]$ species. This mechanistic hypothesis seems reasonable in view of the known properties of monomeric $[Pt(PPh_3)_2]$.[3] While this kinetic study sheds light on the reactivities of the platinum(0) complexes, it does not provide any information germane to the actual insertion of platinum into the carbon–carbon bond of the cyclobutenedione.

Reactions of 3-*Phenylcyclobutene*-1,2-*dione*.—Reaction of 3-phenylcyclobutene-1,2-dione, (IIIa), with platinum(0) complexes gave either the alkene complex (Va) or the platinacyclopentene derivative (IVa), depending on the experimental conditions. As the alkene complex (Va) can be isolated in a pure state, it is possible to monitor the kinetics of the reaction (Va) to (IVa) as well as the sequence (IIIa) to (Va) to (IVa). If generation of $[Pt(PPh_3)_2]$ is rate determining here, as in the reaction with (I), the first-order rate constants for the reactions of $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ with (IIIa) and (I) should be the same, under identical conditions. In chloroform at 298 K, the rate constant for the reaction of $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ with (I) is 4.5×10^{-4} s^{-1}, and rate constants for the reaction of the complex with various excesses of phenylcyclobutenediones lie between 2.9×10^{-4} and 3.4×10^{-4} s^{-1}. These latter rate constants are estimates from observed initial rates; the rate of the subsequent insertion reaction is only *ca.* ten times slower than that of the initial reaction of the complex. The similarity of the rate constants for the two reactions suggests that they have a common rate-determining step, loss of diphenylacetylene from the platinum.

The kinetics of the rearrangement (redox isomerisation) of the alkene complexes (Va) to the platinacyclopentene (IVa) were examined in a range of solvent and temperature in order to determine the kinetic parameters. From the kinetic observations we also attempted to establish the mechanisms for oxidative insertion of platinum into the carbon–carbon bonds of cyclobutenediones. The reactions followed first-order kinetics accurately over

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* The uncertainties represent 90% confidence limits.

[3] J. Halpern and T. A. Weil, *J.C.S. Chem. Comm.*, 1973, 631 and refs. therein.

at least three half-lives under all conditions in this investigation. Observed first-order rate constants for the reaction of the alkene complex (Va) are in Table 2. Activation parameters are reported in Table 3.

TABLE 2

Observed first-order rate constants (k) for the isomerisation of complex (Va) (*ca.* 10^{-2} mol dm^{-3})

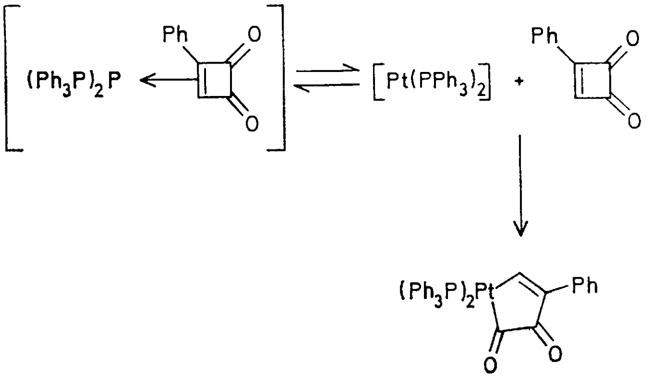
Chloroform		Benzene		Toluene		Benzyl alcohol	
T/K	10^5k/s^{-1}	T/K	10^5k/s^{-1}	T/K	10^5k/s^{-1}	T/K	10^5k/s^{-1}
298.5	4.2	299.6	1.1	308.2	11.2	308.2	8.4
298.8	2.6	303.5	2.1				
299.6	4.4	307.8	5.0				
300.6	3.5	308.4	5.4				
303.4	6.5	312.3	14.0				
303.4	6.5	314.4	14.6				
308.4	11.5	317.2	23.2				
308.4	11.8						
312.3	21.5						
312.3	20.4						
313.7	20.2						
314.4	22.1						
317.2	37.4						
317.2	41.3						
317.3	37.9						
318.4	35.6						

TABLE 3

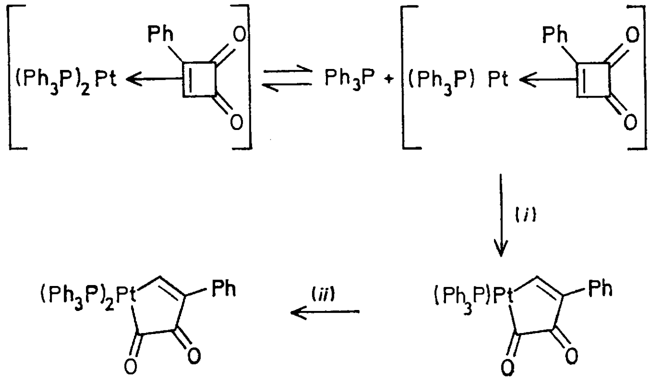
Activation parameters for the isomerisation of complex (Va) in chloroform and benzene; the uncertainties cited are those for the 90% confidence limits

Solvent	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Chloroform	98 ± 4	-3 ± 13
Benzene	138 ± 7	122 ± 25

If the mechanism of the rearrangement is intramolecular, one would expect an activation entropy close to zero. One would also expect only a small variation of rate with variation in solvent. The activation entropy for the reaction in chloroform solution is indeed zero within experimental uncertainty, but the activation entropy in benzene solution is markedly positive. These observations suggest that, although the expected intramolecular mechanism operates in chloroform, a dissociative mechanism may operate in benzene. In the latter case, two possibilities exist. (*a*) Rate-determining loss of $[Pt(PPh_3)_2]$ from the complex followed by rapid insertion of this species into a C–C σ bond of the cyclobutenedione ring (Scheme 1). Such a dissociation of a platinum(0) alkene complex has often been suggested. Indeed, the dissociation constant of the complex $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ has been determined,[4] although subsequently the interpretation of the spectrophotochemical evidence suggested very little dissociation of this complex.[5] There is a precedent for our suggestion of insertion of Pt^0 into a C–C σ bond in the reaction of $[Pt(PPh_3)_4]$ with 1,1,2,2-tetracyanocyclopropane.[6] (*b*) Loss of one PPh_3 unit, rapid rearrangement of the remainder of the complex, followed by recombination of the PPh_3 to the ring-expanded system (Scheme 2). This mechanism has a precedent in the reported isomerisation of $[Pt(C_2Cl_4)(PPh_3)_2]$ to the vinyl complex $[Pt(ClC{=}CCl_2)Cl(PPh_3)_2]$.[7]



SCHEME 1



SCHEME 2 (*i*), − PPh_3; (*ii*), + PPh_3

In balance we prefer the mechanism in Scheme 1 over that in 2. The postulated difference in mechanism in different solvents also has a parallel in the isomerisation of the aforementioned alkene complex $[Pt(C_2Cl_4)(PPh_3)_2]$, whose mechanism is thought to be different in benzene solution from that in other solvents.[7] In this case the difference in mechanism was attributed to the specifically favourable solvation of triphenylphosphine by benzene, encouraging reversible loss of PPh_3 from $[Pt(C_2Cl_4)(PPh_3)_2]$. In the present rearrangement of (Va) to (IVa) we suggest that favourable solvation of the PPh_3 portions of the $[Pt(PPh_3)_2]$ entity may encourage dissociation of the latter from the alkene in benzene solution, thus permitting a dissociative mechanism for the rearrangement.

Reactions of other Cyclobutenediones.—Reactions of 3,4-dimethoxycyclobutene-1,2-dione, (IIIc), and of 4-methoxy-3-phenylcyclobutene-1,2-dione, (IIIb), with

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[4] A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1963, **41**, 1235; J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491.

[5] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.

[6] M. Lenarda, R. Ros, M. Graziani, and U. Belluco, *J. Organometallic Chem.*, 1974, **65**, 407; D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Organometallic Chem.*, 1974, **70**, 133.

[7] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **15**, 217.

$[\mathrm{Pt(PhC{\equiv}CPh)(PPh_3)_2}]$ both yielded the platinacyclopentene derivatives (IVc) and (IVb). It proved impossible to isolate, or even detect, alkene intermediates in these reactions. The kinetic pattern for these reactions is first-order, with rate constants of 3.3×10^{-4} and 5.1×10^{-4} $\mathrm{s^{-1}}$ in chloroform at 298 K respectively. The similarity of these rate constants to those for the reaction of $[\mathrm{Pt(PhC{\equiv}CPh)(PPh_3)_2}]$ with benzo- and with phenylcyclobutenedione is consistent with rate-determining dissociation of diphenylacetylene in each case.

EXPERIMENTAL

Benzocyclobutene-1,2-dione,[8] 3-phenylcyclobutene-1,2-dione,[9] 4-methoxy-3-phenylcyclobutene-1,2-dione,[10] 3,4-dimethoxycyclobutene-1,2-dione,[11] 4-methyl-3-phenylcyclobutene-1,2-dione,[12] $[\mathrm{Pt(PhC{\equiv}CPh)(PPh_3)_2}]$,[13] and $[\mathrm{Pt(}$*trans*$\mathrm{\text{-}PhCH{=}CHPh)(PPh_3)_2}]$ [14] were prepared as described in the literature.

Kinetics.—The kinetic runs were carried out in 1 cm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer; optical densities were monitored at 523 nm for the benzocyclobutene-1,2-dione reactions and at 490 nm for all the others. Rate constants, and thence activation parameters, were computed (PDP 11) using a standard least-mean-squares program.

We thank the Royal Society for a Grant-in-aid for the purchase of the spectrophotometer, the S.R.C. for support, Johnson, Matthey Ltd. for the loan of chemicals, and Dr. G. F. Everitt for carrying out preliminary experiments.

[5/884 *Received*, 9*th May*, 1975]

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[12] W. Ried and H. Kohl, *Synthesis*, 1971, 542.

[13] A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1964, **42**, 1063.

[14] J. Chatt, B. L. Shaw, and A. A. Williams, *J. Chem. Soc.*, 1962, 3269.