

the more drastic cleaning procedures minimize the magnitude of this peak. Nominally, the count rate is an order of magnitude below the chemisorbed oxygen count rate.

The binding energies for the various oxides of platinum could be determined from known samples. For example, PtO is prepared by partial oxidation of platinum foil exposed to oxygen (15 atm) at 300°. The binding energies for the 4f electrons are shifted to 73.4 and 76.6 eV. The values for PtO<sub>2</sub>·H<sub>2</sub>O (Adam's catalyst) are further shifted to 74.5 and 77.8 eV in excellent agreement with the shifts reported by Delgass.<sup>1</sup> With known spectra for four platinum species, the spectra for chemically oxidized surfaces can be readily interpreted. For example, data in Table I illustrate the resolved spectrum for a nitric acid oxidized substrate. Known values of binding energies for Pt, PtO<sub>ads</sub>, and PtO are used in the deconvolution while the value for the PtO<sub>2</sub> species is determined from the best fit.

The electrochemically formed oxides are prepared potentiostatically in 1 M HClO<sub>4</sub> using a surface pretreated *via* aqua regia followed by FeSO<sub>4</sub> reduction. After several minutes of electrolysis, the electrode is removed from the cell, rinsed thoroughly in nitrogen-saturated distilled water, and immediately placed in the ESCA sample chamber. Binding energies for the electrochemically formed oxides could be determined from the sequence of spectra shown in Figure 1. For example, Pt and PtO<sub>ads</sub> peak values can be obtained in Figure 1a. Using these values in Figures 1b and c the remaining binding energies can be found and compared to knowns for chemical identification. These results are given in Table I. For each of the four species, the peak area ratios for Pt 4f (<sup>5/2</sup>) to 4f (<sup>7/2</sup>) are near 1.33. Note that at the +1.2 V oxidation potential, both Pt and chemisorbed oxygen are observed, in general agreement with many oxidation mechanisms.<sup>9</sup> Above +1.6 V, the relative concentration of PtO<sub>2</sub> begins to increase until it becomes the predominate species at +2.2 V. These results conclusively reveal the presence of discrete stoichiometric platinum oxides on the electrode surface and represent the most definite spectroscopic evidence yet available to confirm their existence.

ESCA is clearly a valuable tool for examining in a semiquantitative manner the composition of complicated thin films. The direct observation of chemisorbed species along with binding energy shifts of surface substrates may yield the intricate details regarding electronic reorganization in the bonds. Comparison of ESCA data to other results, especially low-energy electron diffraction<sup>10</sup> data, may further aid in understanding chemisorption. In addition the technique appears directly applicable to chemically analyzing electrodes which have been electrochemically altered or covered with electrogenerated reaction products. Further studies regarding these items are in progress.

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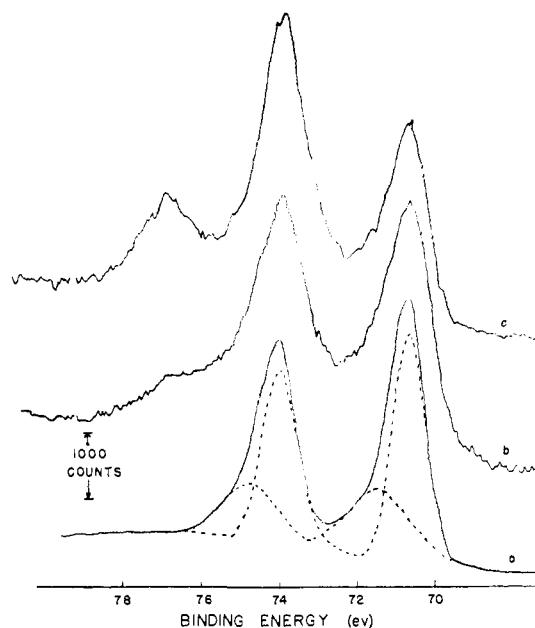


Figure 1. Platinum 4f electron spectra of platinum foil pretreated *via* (a) hydrogen reduction at 400° for 10 hr and hydrogen desorption at 400° (10<sup>-5</sup> mm) for 5 hr followed by adsorption of pure oxygen (1 atm) at ambient temperature, (b) electrochemical oxidation at +1.2 V, and (c) +2.2 V *vs.* sce in 1 M HClO<sub>4</sub>. Curves b and c have been displaced upward.

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### A Thermochemical Probe into the Mechanism of Electrophilic Addition to Olefins

Sir:

Most of the evidence concerning the mechanism of electrophilic addition to olefins, particularly bromination, has come either from kinetic measurements<sup>1</sup> (substituent effects) or from product analyses<sup>2</sup> (stereochemistry and regioselectivity). However, it has proved difficult to obtain unequivocal evidence about the nature of the cationic intermediates (or the transition states which precede, and presumably closely resemble them). For a long time such additions were considered to be generally stereospecific and *trans*, which was explained in terms of the well-known cyclic bromonium ion intermediate proposed by Roberts and Kimball,<sup>3</sup> but it is now clear that polar bromine additions can show quite variable stereoselectivity, ranging all the way from predominant *cis* to exclusive *trans* addition.<sup>4</sup> Thus, the nature of the intermediates has been shown to depend strongly on the structure of the starting olefin, and it is now more

(1) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Elmsford, N. Y., 1966, pp 114-128, and references cited therein.

(2) Reference 1, pp 130-146; R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(3) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937).

(4) J. H. Rolston and K. Yates, *ibid.*, **91**, 1477 (1969).

(8) P. Grandadam, *Ann. Chim.*, **4**, 83 (1935).

(9) (a) A. K. N. Reddy, M. A. Genshaw, and J. O'M Bockris, *J. Chem. Phys.*, **48**, 671 (1968); (b) R. Thacker and J. P. Hoare, *J. Electroanal. Chem.*, **30**, 1 (1971).

(10) J. W. May, *Advan. Catal.*, **21**, 152 (1970).

**Table I.** Heats of Combustion of Isomeric Olefins

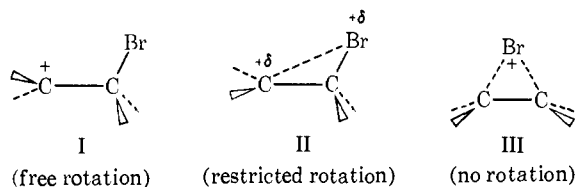
Olefin	$\Delta H$ combustion, <sup>a,b</sup> kcal mol <sup>-1</sup>	$\Delta H^{\ddagger}$ isomerization, kcal mol <sup>-1</sup>
<i>cis</i> -Diisopropylethylene	-1260.46 ± 0.28	1.96 ± 0.30
<i>trans</i> -Diisopropylethylene	-1258.50 ± 0.12	
<i>cis-tert</i> -Butylethylethylene	-1263.97 ± 0.17	5.12 ± 0.38
<i>trans-tert</i> -Butylethylethylene	-1258.85 ± 0.34	
<i>cis</i> -Stilbene	-1769.61 ± 0.18 <sup>c</sup>	
<i>trans</i> -Stilbene	-1759.32 ± 0.12 <sup>c</sup>	3.08 ± 0.22 <sup>e</sup>

<sup>a</sup> All values are the means of at least five determinations. <sup>b</sup> Errors quoted are standard deviations of the mean. <sup>c</sup> From J. Coops and G. J. Hoijtink, *Recl. Trav. Chem. Pays-Bas*, **69**, 538 (1950). <sup>d</sup> Errors quoted are standard deviations of the difference. <sup>e</sup> Value corrected for latent heat of fusion of the trans isomer.

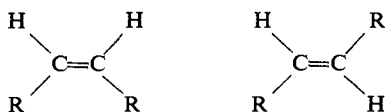
**Table II.** Rate Constants and Activation Parameters

Olefin	$10^{-2}k_2, M^{-1} \text{sec}^{-1}$					$\Delta H^{\ddagger}$ , kcal	$\Delta S^{\ddagger}$ , eu
	18.2°	25.1°	32.3°	38.4°	44.5°		
<i>cis</i> -Diisopropylethylene	2.08	2.68	4.56	5.36	6.03	6.96 ± 0.53	-23.9 ± 1.7
<i>trans</i> -Diisopropylethylene	4.80	6.37	7.79	10.04	12.53	6.00 ± 0.28	-25.6 ± 1.0
<i>cis-tert</i> -Butylethylethylene	7.28	11.17	11.76	16.53	21.08	6.56 ± 0.53	-22.9 ± 1.8
<i>trans-tert</i> -Butylethylethylene	3.31	4.75	6.47	7.91	9.12	6.27 ± 0.32	-25.3 ± 1.0
	$10^2k_2, M^{-1} \text{sec}^{-1}$						
	25.1°	30.4°	35.2°	43.1°			
<i>cis</i> -Stilbene	5.44	7.45	10.9	19.8		12.78 ± 0.45	-21.5 ± 1.5
<i>trans</i> -Stilbene	1.84	2.62	3.40	6.43		12.49 ± 0.49	-24.1 ± 1.6

reasonable to propose a spectrum of possible ionic intermediates, of which I and III are extremes.



Since product stereochemistry alone does not give unequivocal information as to the extent of bromine bridging in the ionic intermediates, we have been interested in developing alternative methods of assessing the importance of cyclic bromonium ion structures and now wish to report some preliminary results using a combined thermochemical kinetic approach. In comparing symmetrically disubstituted *cis*- and *trans*-olefins, the considerable difference in steric interactions between the groups R is reflected in the heats of combustion of the isomers. The *cis* group interactions result in values of  $\Delta H_c$  for the *cis* isomers which are



higher than those for the *trans* by about 1–10 kcal for typical olefins.<sup>5</sup> It is therefore of interest to try to determine to what extent these steric differences are retained in the transition states for electrophilic addition. If the transition state resembles I, the steric repulsions in the *cis* case could easily be relieved by a small rotation of the C–C bond, thus reducing the ground-state enthalpy difference between *cis*- and *trans*-olefin.

(5) H. F. Bartolo and F. D. Rossini, *J. Phys. Chem.*, **64**, 1685 (1960), and references cited therein.

If the transition state resembles III then the steric repulsion difference between *cis*- and *trans*-olefin would be accentuated as the groups R are forced together due to a combination of hybridization and bond-length changes.<sup>6</sup> We have, therefore, attempted to use a combination of  $\Delta H_c$  and  $\Delta H^{\ddagger}$  values to assess the probable extent of bromine participation at the transition state, using several pairs of geometrically isomeric olefins.

Enthalpies of combustion were measured using a Parr oxygen bomb calorimeter equipped with an automatic adiabatic temperature control system. All determinations, including calibration experiments, were carried out using standard techniques and the results were corrected to standard conditions using the Washburn correction terms.<sup>7</sup> The enthalpies of combustion

are listed in Table I and refer to 25° and 1 atm for the liquid state. It can be seen that in each case the *cis* isomer is less stable than the *trans*, the values of  $\Delta H_{\text{isom}}$  reflecting mainly steric effect differences between the various neighboring groups.

The rates of bromination of the dialkylethylenes were measured as a function of temperature using a Durrum-Gibson stopped-flow kinetic spectrometer equipped with a storage oscilloscope. Measurements on the stilbenes were made on a Cary 16 spectrophotometer using 10-cm cells. Anhydrous acetic acid was used as solvent and 490 m $\mu$  was chosen to monitor the disappearance of bromine. Initial bromine concentrations were in the range  $2\text{--}5 \times 10^{-4} M$  so that only the simple first-order term<sup>8</sup> in  $[\text{Br}_2]$  contributes significantly to the rates. For each run, olefin concentrations were in at least 40-fold excess, thus yielding pseudo-first-order rate constants. Rate measurements were made at four–five temperatures in the range 18–45° and from two to four runs were carried out at each temperature. Activation parameters were obtained from the slopes and intercepts of plots of  $\log k/T$  vs.  $1/T$  using a linear least-squares program. The kinetic results are given in Table II, the errors quoted being standard deviations. In each of the three cases listed in Table II, the *cis* isomer has the higher value of  $\Delta H^{\ddagger}$  and the less negative  $\Delta S^{\ddagger}$  value. Although these differences in  $\Delta H^{\ddagger}$  between *cis*- and *trans*-olefin are not

(6) Calculations using the known geometries of *cis*-2-butene and 2,3-dibromobutane show that the methyl–methyl distance decreases from 2.99 to 2.70 Å, respectively, if we consider the latter compound in the *cis*-staggered conformation. In an intermediate bromonium ion we would expect the methyl–methyl distance to be intermediate between these values and thus to have decreased, assuming no rotation about the C–C bond.

(7) E. W. Washburn, *J. Res. Nat. Bur. Stand.*, **10**, 525 (1933).

(8) I. K. Walker and P. W. Robertson, *J. Chem. Soc.*, 1515 (1939); see also, J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332, (1970).

large in comparison with the standard deviations in each  $\Delta H^\ddagger$  value, the very similar  $\Delta H^\ddagger$  values for each pair of isomers nevertheless demonstrate that the ground-state enthalpy differences of between 2 and 5 kcal are not significantly changed<sup>9</sup> at the transition state and are probably somewhat increased. Since ground-state steric effects appear to be retained,<sup>10</sup> if not actually increased at the transition state, this indicates a lack of free rotation about the C-C bond and is more consistent with cyclic bromonium ion formation than with development of an open  $\alpha$ -bromocarboxonium ion. Product studies support this conclusion. The *cis*-diisopropylethylene yields only racemic *dl*-dibromide. Neither the *meso*-dibromide nor the acetoxy bromide, which were independently synthesized, could be detected in the products by glc. The *trans*-olefin under identical conditions gives the *meso*-dibromide as predominant product, no detectable *dl*-dibromide, some acetoxy bromide, and unidentified material. Thus both olefins add bromine predominantly, if not completely, *trans*.

We are currently investigating pairs of unsymmetrical olefins which are known<sup>4,11</sup> not to give stereospecific *trans* addition in acetic acid, such as alkyl-substituted styrenes, and also symmetrical alkenes, which have even larger ground-state effect differences, such as the *cis*- and *trans*-di-*tert*-butylethylenes.<sup>12</sup>

(9) The enthalpies of isomerization quoted in Table I refer to the pure liquid state while the activation enthalpies refer to acetic acid solution. However, it seems unlikely that the enthalpies of solution for geometrical isomers will differ by an amount greater than experimental error in the  $\Delta H^\ddagger$  values (see H. Herzog, Ph.D. Thesis, University of Paris, 1968, and J. E. Dubois and H. Herzog, unpublished results).

(10) A referee has pointed out that in two of the three cases above, the *cis* isomer reacts faster than the *trans*, and that this could be interpreted in terms of relief of steric strain. However, it is dangerous to draw such conclusions from simple rate differences of this magnitude since these only represent about 0.5 kcal in free energy. In the case of the *cis-tert*-butylethylene which reacts twice as fast as the *trans*-, it is the fact that the large ground-state enthalpy difference of more than 5 kcal is at least retained at the transition state which is significant.

(11) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969); R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968).

(12) R. D. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958); J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961).

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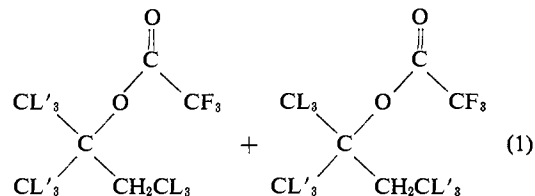
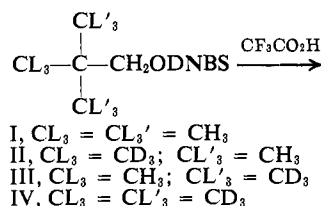
## Lack of Methyl Participation in a Neopentyl Arylsulfonate Solvolysis

Sir:

We have obtained relatively direct evidence that the methyl migration step and the rate-controlling step in the solvolysis of neopentyl 2,4-dinitrobenzenesulfonate in 97.3% trifluoroacetic acid are not the same. A further inference is that there is no methyl participation in the rate-controlling step. The method used consists of a comparison of the kinetic isotope effects produced by successive replacement of  $\beta$ -CH<sub>3</sub> by  $\beta$ -CD<sub>3</sub> with the extent of CH<sub>3</sub>-CD<sub>3</sub> migration in the solvolyses of II and III.<sup>1</sup>

Trifluoroacetic acid was chosen as the solvent because (a) there is a pronounced accelerating effect of

(1) (a) W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969); (b) *ibid.*, in press.



$\beta$ -CH<sub>3</sub> (at 75°,  $k_{\text{NeopOTs}}/k_{\text{EtOTs}} = 480$  in CF<sub>3</sub>CO<sub>2</sub>H and 1/1750 in EtOH)<sup>2</sup> which has been attributed to participation in the C-O heterolysis step, and (b) a single product, *tert*-amyl trifluoroacetate, is formed.<sup>2</sup> For practical reasons, 97.3% CF<sub>3</sub>CO<sub>2</sub>H containing 0.17 M CF<sub>3</sub>CO<sub>2</sub>Na was settled upon.<sup>3,4</sup> A fast leaving group also was required.<sup>4</sup>

First-order rate constants were determined by following the change in ultraviolet absorbance at 273 m $\mu$  of solutions *ca.*  $2 \times 10^{-4}$  M in substrate.<sup>1,2</sup> The results, Table I, show that there is no significant kinetic isotope

Table I. First-Order Rate Constants,  $10^4k$  (sec<sup>-1</sup>), in 97.3% CF<sub>3</sub>CO<sub>2</sub>H-0.17 M CF<sub>3</sub>CO<sub>2</sub>Na<sup>a,b</sup>

Compd	30°	40°	50°
I	2.03 ± 0.02	6.32 ± 0.08 <sup>c</sup>	18.4 ± 0.2
II		6.32 ± 0.02	
III		6.12 ± 0.06	
IV	1.99 ± 0.06	6.15 ± 0.11 <sup>c</sup>	18.1 ± 0.1

<sup>a</sup> Average of three-five kinetic runs, except where indicated.

<sup>b</sup> Average deviations listed. <sup>c</sup> Twelve runs.

effect. Other neopentyl derivative solvolyses also have little or no  $\gamma$ -*d* kinetic isotope effect.<sup>1a,5</sup>

Extents of CH<sub>3</sub> to labeled methyl migration in the samples of compounds II and III were determined by nmr, Table II. With an HA-100, 16 scans of the nmr

Table II. Relative Product  $\gamma$ -H Areas in 97.3% CF<sub>3</sub>CO<sub>2</sub>H-0.17 M CF<sub>3</sub>CO<sub>2</sub>Na at 40°<sup>a,b</sup>

I	II	III
100.24 ± 0.40	74.23 ± 1.36	41.56 ± 0.39

<sup>a</sup>  $\gamma$ -H areas of product solutions relative to a value of 100 for the Ar-H areas. <sup>b</sup> Standard deviations are listed.

spectrum of each solution, about 0.1 M in substrate, were made over the period 8-12 half-lives of the solvolysis and recorded in a Varian C-1024 time averaging computer.<sup>6</sup> The data were then transferred to a DEC PDP-12 computer in which the isolated  $\gamma$ -hydrogen

(2) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969).

(3) The ultraviolet spectral change in 100% CF<sub>3</sub>CO<sub>2</sub>H was too small for accurate rate determinations.

(4) In the time of 20 half-lives of the solvolysis of I, *tert*-amyl trifluoroacetate (0.1 M) in 97.3% CF<sub>3</sub>CO<sub>2</sub>D-0.17 M CF<sub>3</sub>CO<sub>2</sub>Na suffered less than 2%  $\gamma$ -D incorporation.

(5) For neopentyl methanesulfonate in water,  $k_{\gamma\text{-H}_3}/k_{\gamma\text{-D}_3} = 1.017$ ; M. J. Blandamer and R. E. Robertson, *Can. J. Chem.*, **42**, 2137 (1964).

(6) There was no detectable  $\gamma$ -hydrogen exchange over this time period, but  $\beta$ -hydrogen exchange was extensive.<sup>4</sup>