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### Photocalorimetry. Enthalpies of Photolysis of *trans*-Azobenzene, Ferrioxalate and Cobaltioxalate Ions, Chromium Hexacarbonyl, and Dirhenium Decarbonyl

Sir:

We report here on a new type of calorimetry, *photocalorimetry*. The procedure determines the ordinary  $\Delta H$  of a reaction, but is special in that the reaction is light induced. If light of flux  $F^\circ$  (defined here as  $\text{J s}^{-1}$ ) is absorbed by a solution, then in the absence of photochemical (or thermal) reaction and of emission, the energy  $F^\circ t$  must appear as heat, where  $t$  is the time of irradiation in seconds. If, however, a photoinduced reaction occurs, the observed rate of heat production will be some different value,  $F$ , and the quantity  $(F^\circ - F)t$  gives the enthalpy change associated with the amount of reaction that has occurred. The  $\Delta H$  of reaction may be calculated as  $(F^\circ - F)/n$ , where  $n$  is the moles of such reaction per second. Alternatively, the fractional discrepancy due to the heat of reaction is  $f = (F^\circ - F)/F^\circ$ ; if positive,  $f$  is the efficiency of conversion of light to chemical energy. Further, if monochromatic light is used,  $\Delta H = fE/\phi$ , where  $E$  is the energy per mole of light quanta, and  $\phi$ , the quantum yield for the photoreaction. Note that if the experimental  $n$  is used in calculating  $\Delta H$ , the result will be correct even if absorption by the cell window or by photoproducts occurs, although  $f$  and  $\phi$  will be low.

Photocalorimetry suffers in precision because it depends on the difference  $(F^\circ - F)$  and is insensitive if  $\phi$  is small. It can, however, be a convenient alternative to other methods of  $\Delta H$  determination, and in some cases may be the only practical

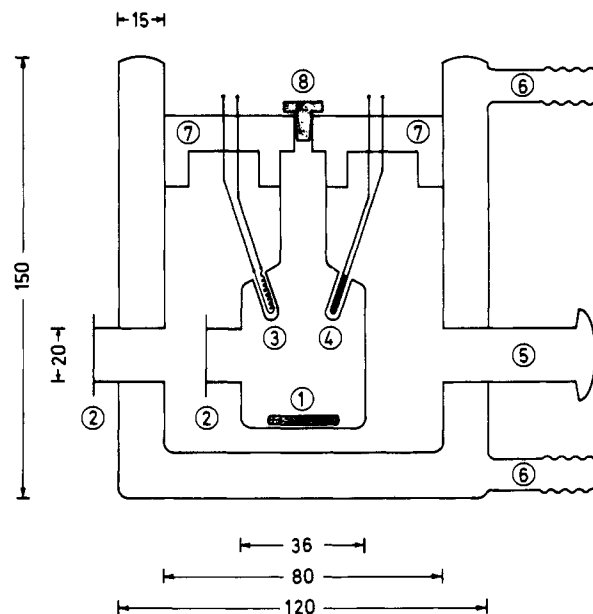


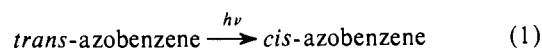
Figure 1. Photocalorimeter cell (dimensions in mm): (1) coated magnetic stir bar, (2) quartz windows, (3) heating coil, (4) thermistor, (5) to vacuum pump, (6) to thermostat, (7) metal cover, (8) cap to inner cell.

method. Certainly, current thermochemical complications<sup>1-3</sup> allow rather few enthalpies of reactions between organometallic compounds in solution to be assembled; the same is true for kinetically stable Werner-type coordination compounds. A further point is that there can be cases where the photochemical reaction is complex or not fully understood, and yet is one for which the enthalpy change is desired. Potential solar energy storage reactions may fall in this category.<sup>4</sup> The equipment described here is well suited to the testing of such systems since  $f$  is determined.

The essential features of our equipment and procedure are as follows. The photocalorimeter cell is shown in Figure 1. The inner cell is magnetically stirred and its temperature is sensed by a thermistor and associated bridge and chart recorder. A precise amount of electrically generated heat can be delivered by means of a resistance coil, using a constant current generator. The space around the cell is evacuated and the outer space thermostated. The cover is of heat-conducting metal, effectively to complete the constant temperature environment. Monochromatic light, controlled by a shutter, is used. Many of the features of the equipment are similar to those for the calorimetric determination of fluorescence yields.<sup>5</sup>

An experiment consisted of the following sequence. The cell was first filled with an absorbing but nonphotoactive reference solution, and the heat capacity,  $C$ , determined as joules per chart division (the chart readout being proportional to temperature). The rate of light heating,  $R$ , was determined by opening the shutter for the appropriate time and is reported in chart divisions per second. The product  $CR$  gives  $F^\circ$ . The cell was then rinsed and filled with the solution of interest,  $C$  and  $R$  again determined, and thus  $F$ . While not in principle necessary, we made the practice of using as reference solution a similar, but nonphotoactive system in the same solvent. Irradiations were sufficiently limited to avoid significant secondary photolysis; none of our solutions emitted to any visually detectable extent; the data are for temperatures falling in the range 24.5-25.5 °C.

The results for the five reactions studied are summarized in Table I. Since the method was new, it was desirable to see if a known  $\Delta H^\circ$  could be confirmed. The reaction chosen is



**Table I.** Photocalorimetric Enthalpies of Reaction at 24.5–25.5 °C

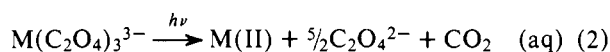
Substance	Reaction <sup>a</sup>	Solvent	$\lambda$ , nm	$10^4 C$ , <sup>b</sup> J div <sup>-1</sup>	$10^4 R$ , <sup>b</sup> div s <sup>-1</sup>	Flux $10^4 F^\circ$ or $F$	$10^7 n^c$ mol s <sup>-1</sup>	$\phi$	$f$ , %	$\Delta H^\circ$ , <sup>d</sup> kcal mol <sup>-1</sup>
<i>trans/cis</i> -Azobenzene <sup>e</sup>	Ref	<i>n</i> -Heptane	546	1190 ± 13(5)	5972 ± 52(6)	710.7				
<i>trans</i> -Azobenzene	1	<i>n</i> -Heptane	546	1238 ± 12(4)	5166 ± 47(5)	639.6		0.448 <sup>f</sup>	10.0	11.7 ± 1.3
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	Ref	0.01 M HClO <sub>4</sub>	446	2636 ± 23(6)	3901 ± 34(6)	1028				
Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>3-</sup>	2	0.1 M H <sub>2</sub> SO <sub>4</sub>	446	2680 ± 21(5)	4584 ± 37(4)	1229	3.75	0.98 <sup>g</sup>	-19.6	-12.8 ± 0.7
Co(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>3-</sup>	2	0.01 M HClO <sub>4</sub>	446	2735 ± 12(3)	3800 ± 17(3)	1039	0.51	0.132 <sup>h</sup>	-1.1	-5.2 ± 4.4
Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	Ref	Cyclohexane	366	1174 ± 5(4) 1204 ± 6(3)	18560 ± 240(5) 18090 ± 72(3)	2179 <sup>i</sup> 2178 <sup>i</sup>				
Cr(CO) <sub>6</sub>	3	0.04 M pip <sup>j</sup>	366	1179 ± 3(4)	18400 ± 126(4)	2169	1.90	0.58 <sup>k</sup>	0.4	1.1 ± 2.7
Re <sub>2</sub> (CO) <sub>10</sub>	4	0.0073 M I <sub>2</sub>	366	1188 ± 3(4)	19410 ± 24(4)	2306	1.95	0.49 <sup>l</sup>	-5.9	-15.6 ± 2

<sup>a</sup> Numbers refers to equations in text. Ref denotes nonphotoreactive reference solution. <sup>b</sup> Standard deviations; number in parentheses gives number of runs. Actual heating and irradiation times were in the range of 20 to 180 s. <sup>c</sup>  $n$  values determined spectrophotometrically by the decrease in absorption at 466 nm for system 2, the increase at 420 nm for system 3, and the decrease at 525 nm for system 4. <sup>d</sup> Propagated probable error. <sup>e</sup> *Trans/cis* mixture photostationary to 546-nm light. <sup>f</sup> As determined in a separate experiment. <sup>g</sup> From  $n$  and  $F^\circ$ ; lit. value: 1.01 (V. Balzani and U. Carassiti, "Photochemistry of Coordination compounds," Academic Press, New York, N.Y., (1970). <sup>h</sup> From  $n$  and  $F^\circ$ ; lit. value: 0.12 (see ref in footnote g). <sup>i</sup> The two series were carried out before and after the runs on reactions 3 and 4. <sup>j</sup> Piperidine. <sup>k</sup> Our conventionally determined value of 0.58 is higher than that from  $n$  and  $F^\circ$  probably because of cell window filming (which makes  $f$  too small, but does not affect  $\Delta H^\circ$ ). In deaerated solution,  $\phi$  rose to 0.63. <sup>l</sup> Our conventionally determined value of 0.49 is higher than that from  $n$  and  $F^\circ$ . See footnote k. There was no effect of deaeration.

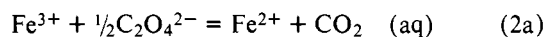
The enthalpy of reaction for the solids is known to be 11.52 ± 0.1 kcal mol<sup>-1</sup> at 25 °C from thermochemical data,<sup>6,7</sup> and the heats of solution in cyclohexane have been reported.<sup>8</sup> Combination of these results gives 11.6 kcal as  $\Delta H^\circ_{298}$  for reaction 1; we assume that essentially the same value applies with *n*-heptane as solvent. The photoreaction has been studied; it reaches a wavelength dependent photostationary state due to back photolysis (the thermal isomerization being quite slow).<sup>9</sup> Since our wavelength of convenience, 546 nm, is at the tail of the visible absorption band, we made a detailed redetermination of the photochemistry, finding 24.8% conversion at 25 °C at the photostationary state,<sup>10</sup> and the forward quantum yield to be 0.448. Our photocalorimetric result of 11.7 × 1.3 kcal for  $\Delta H^\circ_{298}$  is in good agreement with the thermochemical value.

Note that  $f$  is 10% for reaction 1, a light utilization efficiency comparable to that of currently proposed solar energy storage systems (for example,  $f$  is about 8% for norbornadiene → quadricyclene<sup>11</sup>). Further studies of simple and substituted azobenzenes should be worthwhile.

The remaining reactions were chosen for diversity and interest. The ferri- and cobaltioxalate photoreactions are

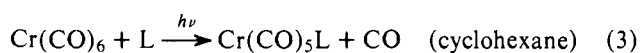


the M(II) product being partially complexed by the oxalate present. We can find no literature values for either system, but if complexation is neglected, we have for M = Fe,



and a  $\Delta H^\circ_{298}$  of -9.8 kcal.<sup>12</sup> This is close to our value for reaction 2. The case of M = Co is included in Table I as an indication that the reaction is nearly thermoneutral. A redetermination at a shorter wavelength (for which the quantum yield would be higher) would reduce the propagated error. The reference solution for these two reactions, aqueous Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, is nearly photoinert at 446 nm.<sup>13</sup>

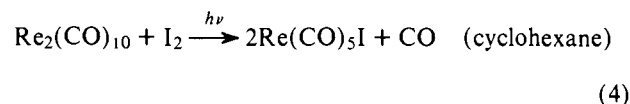
The next reaction chosen is



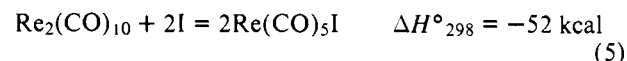
where L is piperidine. The mechanism is one of scavenging of

photoproducted Cr(CO)<sub>5</sub><sup>14-16</sup> and the net reaction provides a measure of the difference in bond energy between a  $\pi$  bond and a purely  $\sigma$  bond. Our result, apparently the first for such a process, shows the reaction to be nearly thermoneutral. The result could reflect Cr-CO bond strengthening in the product, but it does appear that the energetic significance of  $\pi$ -bonding is not large. The reference substance for the 366-nm irradiations, ferrocene, is photoinert.<sup>15</sup>

The last system provides a measure of a metal-metal bond energy, the particular reaction being



The mechanism is one of I<sub>2</sub> scavenging of an Re(CO)<sub>5</sub> intermediate,<sup>16,17</sup> and the net reaction corresponds essentially to the replacement of a Re-Re bond by two Re-I ones. No thermochemical data appear to be in the literature on this or similar reactions. Assuming that the bond dissociation energy of I<sub>2</sub>(g), 36.5 kcal mol<sup>-1</sup>,<sup>11</sup> is the same in cyclohexane solution, eq 4 can be written as



Thus the Re-Re bond strength is less than two Re-I ones by some 50 kcal (again including any reorganization energy, as with reaction 3), which suggests that it is relatively weak.

We plan to extend our investigations using both the present equipment and a more precise differential photocalorimeter.

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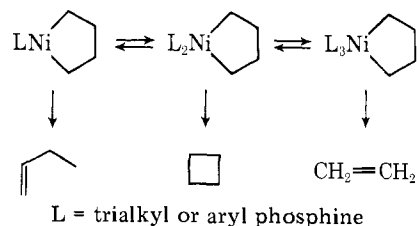
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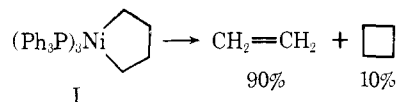
## The Relationship between Metallacyclopentanes and Bis(olefin)-Metal Complexes

Sir:

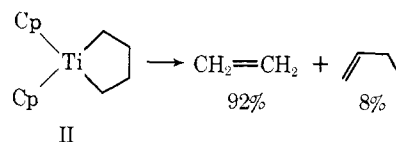
Metallacyclopentanes appear to be intermediates in a number of olefin dimerization reactions.<sup>1,2</sup> We recently reported that phosphine-nickelacyclopentanes decompose by reductive elimination,  $\beta$ -hydride elimination, or C-C bond cleavage depending on the coordination number of the complex.<sup>3</sup>



The most surprising observation was the production of ethylene from the highest coordination number complexes.



Tetramethylenetitanocene (II) also has been observed to decompose to produce ethylene in good yield.<sup>4</sup>



We now have evidence that both of these complexes decompose by reversible carbon-carbon bond cleavage to produce an intermediate bis(ethylene) complex. This process can be detected by labeling two of the equivalent carbons of the metallacycle since the two carbons of the olefin should become equivalent in the intermediate.

Consequently, 2,2,5,5-tetradeuteriometallacycles of nickel and titanocene were prepared. Equilibration of the metallacycle with the bis(olefin) complex should result in the production of the 2,2,4,4- and 3,3,4,4-*d*<sub>4</sub> isomers (Scheme I). Hydride rearrangements would result in the production of isomers containing only one deuterium per carbon.<sup>5</sup>

Since the bromination and protonolysis of metallacycle produces quantitative yields of 1,4-dibromobutane or butane,<sup>3,4</sup> the labeling of the metallacycle can be analyzed by determining

Table I. Isomerization of Phosphine-Nickelacyclopentane in Toluene

Compd	Temp, °C	Time, h	Butane- <i>d</i> <sub>4</sub> , mol % <sup>a</sup>				% isom <sup>c</sup>	% dec
			1,1,4,4	1,1,3,3	2,2,3,3	Others <sup>b</sup>		
1. III- <i>d</i> <sub>4</sub> <sup>e</sup>	10	1	98.3	0	0	1.7	0	
2. I- <i>d</i> <sub>4</sub> <sup>f</sup>	-30	0	95.2	2.4	1.2	1.2	4.8 (3.6 <sup>d</sup> )	0
3. I- <i>d</i> <sub>4</sub> <sup>f</sup>	0	0.5	84.3	7.0	2.6	6.0	13.2 (13.3) <sup>d</sup>	7.4
4. I- <i>d</i> <sub>4</sub> <sup>f</sup>	0	1.0	47.0	29.7	16.1	7.2	66.7 (65.1) <sup>d</sup>	17.0
5. I- <i>d</i> <sub>4</sub> <sup>f</sup> + 4.5PPh <sub>3</sub>	0	1.0	70.9	15.3	8.1	5.7	33.4	14.8
6. I- <i>d</i> <sub>4</sub> <sup>f</sup> + 6.9PPh <sub>3</sub>	0	1.0	84.7	7.4	3.6	4.3	15.2	13.6
7. I- <i>d</i> <sub>4</sub> <sup>f</sup> + 8.0PPh <sub>3</sub>	0	1.0	89.2	5.9	2.9	2.1	12.0 (13.7) <sup>d</sup>	13.0
8. I- <i>d</i> <sub>4</sub> <sup>g</sup>	25	2.0	9.6	16.7	8.7	65.0	97.4	

<sup>a</sup> Relative product yield of chromatographically pure butane-*d*<sub>4</sub> isomer. <sup>b</sup> These isomers include deuterium-scrambled butane-*d*<sub>4</sub> isomers such as butane-1,1,3,4-, -1,2,3,3-, and -1,2,3,4-*d*<sub>4</sub>. <sup>c</sup> Relative percentage of the nickelacyclopentane isomerization was obtained as follows:

$$\frac{[1,1,3,3] + 2[2,2,3,3]}{[1,1,4,4] + [1,1,3,3] + [2,2,3,3]} \times 100$$

<sup>d</sup> These values were obtained by <sup>1</sup>H NMR analysis of 1,4-dibromobutane-*d*<sub>4</sub> afforded on the reaction of the complex with Br<sub>2</sub>. <sup>e</sup> 0.044 M toluene solution. <sup>f</sup> 0.00231 M toluene solution. <sup>g</sup> 0.054 M toluene solution.

Table II. Isomerization of Titanacenacyclopentane in Toluene

Compd	Temp, °C	Time, h	Butane- <i>d</i> <sub>4</sub> , mol % <sup>a</sup>				% isom <sup>c</sup>	% dec
			1,1,4,4	1,1,3,3	2,2,3,3	Others <sup>b</sup>		
9. II- <i>d</i> <sub>4</sub> <sup>e</sup>	-60	0	84.7	6.8	2.5	6.0	12.6	0
10. II- <i>d</i> <sub>4</sub> <sup>e</sup>	-35	0.5	79.6	9.7	5.1	5.6	21.1	3
11. II- <i>d</i> <sub>4</sub> <sup>e</sup>	-35	1.0	73.0	10.7	5.9	10.4	25.1	~3
12. II- <i>d</i> <sub>4</sub> <sup>e</sup>	-45	3.0	68.0	14.4	7.5	10.0	32.73 (31.2) <sup>d</sup>	~5

<sup>a-d</sup> See comparable footnotes in Table I. <sup>e</sup> 0.08 M toluene solution.