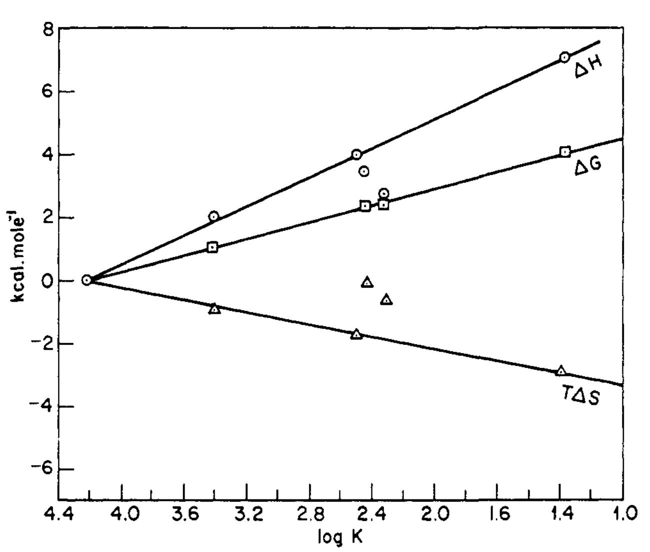

Figure 2. Relative values (to complex V) of ΔG, ΔH, and $T\Delta S$ for Meisenheimer complex formation *vs.* log K for the formation of complexes V–X in methanol at 25°.

cleophilic attack. From the exponential decay of curve 2, the rate constant for the formation of V was calculated to be 10 l. mole^{-1} sec^{-1} at 25°. This value is in reasonable agreement with that obtained by Gold[11] (4 l. mole^{-1} sec^{-1}) under slightly different conditions. The enthalpy of formation of complex I is calculated to be -1.48 ± 0.5 kcal/mole, assuming that the equilibrium constant for its formation is greater than 10^3. The concentration independence of the enthalpy of formation substantiates this assumption.

The free energies, enthalpies, and entropies of formation for complexes V–IX and 1-methoxy-2,4,6-trinitrocylohexadienylide ion (X) are given in Table I.[12] Linear relationships have been found between ΔH, ΔS, and log K as shown in Figure 2. The substituent effects on the enthalpy and entropy of complex formation are large and in opposing directions, resulting, of course, in smaller changes in the free energy. The extent of this type of linear correlation in Meisenheimer complex formation as well as the effects of solvents on the different thermodynamic parameters are under investigation in our laboratories.

Table I. Thermodynamics of Meisenheimer Complex Formation at 25°[a]

Complex	ΔG,[b] kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, eu
V	−5.77	-4.86 ± 0.03[c]	+3.0
VI	−4.66	-2.82 ± 0.47	+6.2
VII	−3.29	-3.41 ± 0.28	−0.40
VIII	−1.36		
VIII[d]	−3.4[e]	-0.82 ± 0.49	+8.7
IX	−2.09	Endothermic	
IX[f]	−3.2	-2.23 ± 0.55	+3.3
X	−1.6	$+2.15 \pm 0.82$	+12.6

[a] In methanol unless stated otherwise. [b] Obtained from spectrophotometric equilibrium constant measurements.[13] [c] The difference between this value and that determined earlier (J. H. Fendler, *J. Am. Chem. Soc.*, **88**, 1237 (1966)) is a reflection of the more precise experimental technique used in the present work. [d] In DMSO–MeOH, 15:85 (v/v). [e] Based on a value of K calculated by the method of T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965). [f] In DMSO–MeOH, 20:80 (v/v).

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(11) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1687 (1964).

(12) The concentrations of the reactants were kept below 0.013 M and the heats of formation were calculated by subtracting the heat of solution of the solid aromatic ether in the appropriate solvent from the heat of solution and reaction in the same solvent containing sodium methoxide. Since the enthalpy of complex formation was calculated using values of K,[6,13] the accuracy of the H values depend on the errors in K.

(13) E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larsen, to be published.

A Novel Effect of Carbon Dioxide on Catalyst Properties. Dimerization of Butadiene

Sir:

While studying the dimerization of butadiene in the presence of nickel, palladium, and platinum complexes, we discovered that carbon dioxide can profoundly alter catalyst properties (see Table I). In the absence of a catalyst, butadiene of course slowly dimerizes to 4-vinyl-1-cyclohexene. This uncatalyzed reaction is not altered by including nitrogen, argon, or carbon dioxide under pressure in the autoclave (expt 1 and 4). With $(Ph_3P)_3Pt$[1] present, the product is still 90–97% 4-vinyl-1-cyclohexene, along with a small amount of 1,3,7-octatriene, provided the autoclave atmosphere is either nitrogen or argon (expt 2, 5, and 7). However, with carbon dioxide present, $(Ph_3P)_3Pt$ converts butadiene mainly to *trans*-1,3,7-octatriene[2] (expt 3, 6, and 8). Catalyst activity is significantly enhanced since the conversions of butadiene are greater when carbon dioxide is present (compare expt 2 and 3, 5 and 6, 7 and 8). The effect of carbon dioxide on the product composition is more pronounced at 95° than at 120° presumably because the competitive thermal dimerization is less favored at the lower temperature (compare expt 7 and 8 with 2 and 3).

Oxygen must be carefully excluded from the system, otherwise the product is mainly 4-vinyl-1-cyclohexene; *cf.* expt 3 with expt 9 where air was deliberately introduced. Probably, with oxygen and carbon dioxide both

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(1) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958); L. Malatesta and R. Ugo, *ibid.*, 2080 (1963).

(2) A detailed structure proof of this material will be published separately by Dr. E. J. Smutny and coworkers. The *trans* isomer content of the triene was >96% as determined by infrared spectroscopy. For a preliminary report on 1,3,7-octatriene see E. J. Smutny, *J. Am. Chem. Soc.*, **89**, 6793 (1967).

Table I. Dimerization of Butadiene[a]

Expt	Catalyst, mmol	Ar, psig	N_2, psig	CO_2, psig	Temp, °C	Convn, %	Product yields,[b] % 1,3,7-OT	4-VCH	1,5-COD	"Others"
1	None			400	120	14	0	100		
2	$(Ph_3P)_3Pt$, 0.5		400		120	18	4	96		
3	$(Ph_3P)_3Pt$, 0.5			400	120	30	68	32		
4	None	400			110	10	0	100		
5	$(Ph_3P)_3Pt$, 0.5	400			110	15	4	96		
6	$(Ph_3P)_3Pt$, 0.5			400	110	21	75	25		
7	$(Ph_5P)_3Pt$, 0.5		400		95	6	3	97		
8	$(Ph_3P)_3Pt$, 0.5			400	95	12	80	20		
9	$(Ph_3P)_3Pt$, 0.5			300 (+100 air)	120	13	20	80		
10	$(Ph_3P)_2(CO_3)Pt$, 0.65			>400	120		17	75		8
11	$(Ph_3P)_2(CO_3)Pt$, 0.65 + Ph_3P, 2.7			>400	120		>68	<32		
12	$(Ph_3P)_2(CO_3)Pt$, 0.65 + Ph_3P, 2.7				120		<32	>68		
13	$(Ph_3P)_4Ni$, 0.45		400		120	71		17	66	17
14	$(Ph_3P)_4Ni$, 0.43			400	120	17		93	7	
15	$[(PhO)_3P]_4Ni$, 0.43				120	87	1	14	82	3
16	$[(PhO)_3P]_4Ni$, 0.43			>400	120	<42		90	8	2

[a] Autoclave (80 ml) experiments. Butadiene, ~16 g (300 mmol); time, 17 hr; solvent, 30 ml of benzene. In expt 12 and 15 the pressure was autogenic, *i.e.*, the autoclave was flushed with nitrogen at atmospheric pressure and then heated. In expt 10, 11, and 16 the gas was introduced into the autoclave to 400 psig and the system subsequently heated; in all other experiments the autoclave was heated to the desired temperature and then the gas was introduced so that the total pressure was 400 psig. [b] Yields are based on converted butadiene. 1,3,7-OT is *trans*-1,3,7-octatriene; 4-VCH is 4-vinyl-1-cyclohexene; 1,5-COD is 1,5-cyclooctadiene; "others" consisted of unidentified butadiene dimers and/or trimers.

present, $(Ph_3P)_3Pt$ is converted to $(Ph_3P)_2(CO_3)Pt$.[3] In the presence of independently synthesized $(Ph_3P)_2(CO_3)Pt$, mainly 4-vinyl-1-cyclohexene was produced from butadiene (expt 10). Interestingly, $(Ph_3P)_2(CO_3)Pt$ with a controlled excess of Ph_3P (~4 mol/mol of catalyst) present does promote the formation of mainly *trans*-1,3,7-octatriene, provided that carbon dioxide is present (expt 11 and 12). Independently, it was demonstrated that the excess Ph_3P converts the carbonato complex to $(Ph_3P)_3Pt$: $(Ph_3P)_2(CO_3)Pt + \text{excess } Ph_3P \rightarrow (Ph_3P)_3Pt + Ph_3PO + CO_2$. Although 400 psig of carbon dioxide was generally employed in the above experiments, 15–30 psig was sufficient to show a significant influence on the product composition.

Results similar to those described above for $(Ph_3P)_3Pt$ were obtained with $(Ph_3P)_4Pd$[4] as the catalyst. The conversion of butadiene increased and *trans*-1,3,7-octatriene became the predominant product when carbon dioxide was introduced.

Carbon dioxide also influences the $(Ph_3P)_4Ni$- and $[(PhO)_3P]_4Ni$-catalyzed dimerization of butadiene. In the absence of carbon dioxide, 1,5-cyclooctadiene is the predominant product[5] (expt 13 and 15), whereas in the presence of carbon dioxide (expt 14 and 16) mainly 4-vinyl-1-cyclohexene is formed. Since with carbon dioxide present the conversion of butadiene is reduced (compare expt 13 and 14) to that level anticipated for thermal dimerization only (expt 1), it appears that the carbon dioxide is almost completely inhibiting the 1,5-cyclooctadiene-producing activity of the nickel catalysts.

At the moment we are unable to propose a reliable mechanism to explain the effects of carbon dioxide. If metal–carbon dioxide complexes are formed *in situ*, they must be rather unstable since all attempts at isolation were unsuccessful. The above results, however, should be of general interest to anyone studying metal catalysis since carbon dioxide is frequently present in reaction systems and catalyst properties may be influenced.

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[3] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Commun.*, 407 (1967); F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *ibid.*, 408 (1967).

[4] L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

[5] G. Wilke, *et al.*, *Angew. Chem.*, **75**, 10 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963).

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Methoxy and Nitro Substituent Effects and Anchimeric Assistance in Solvolysis of Tertiary 2-Methyl-2-benzonorbornenyl *p*-Nitrobenzoates[1]

Sir:

As an indirect criterion for carbon participation in solvolysis of secondary *exo*-2-norbornyl derivatives, Brown has employed the expected rapid attenuation of the *exo*/*endo* rate ratio as a 2-substituent is added and then made increasingly more electron releasing.[2a] This is based on the reasonable supposition that an electron-releasing group will be more rate enhancing for the anchimerically unassisted *endo* derivative than the anchimerically assisted *exo* epimer. However, such substituent effects can be treacherous, since substituents can introduce various steric problems. How treacherous the indirect criterion is has been illustrated by its application by Brown and Tritle to 2-benzonorbornenyl solvolysis.[2b] By introducing methyl and phenyl substituents at C-2 they found that the *exo*/*endo* rate ratio changed from 7500[3a,c] for hydrogen to 6500

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[1] Supported in part by the National Science Foundation.

[2] (a) H. C. Brown, *Chem. Brit.*, 199 (1966); *Chem. Eng. News*, **45**, No. 7, 87 (1967); (b) H. C. Brown and G. L. Tritle, *J. Amer. Chem. Soc.*, **88**, 1320 (1966).

[3] (a) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida,