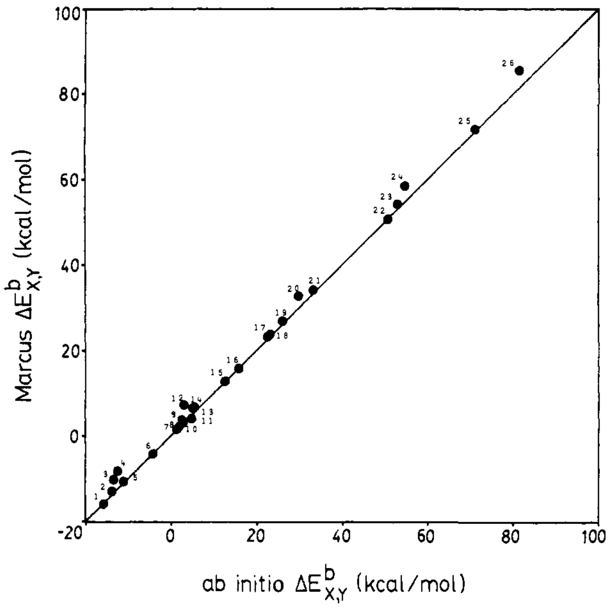

Figure 4. Plot of $\Delta E^b_{X,Y}$, calculated directly from the energy difference between $X^- + CH_3Y$ and the transition structure $[X-CH_3-Y]^-$, vs. the same quantity from eq 4. Data points 1-26 refer to the following (X,Y): (F,SH), (HO,F), (H_2N,F), (H,F), (F,OOH), (CH_3O,F), (F,CN), (F,OCH_3), (HO,CN), (HOO,F), (HCC,F), (H,CN), (H,OH), (F,OH), (NC,F), (HS,F), (F,CCH), (H,CCH), (H,NH_2), (F,NH_2), (NC,OH), (H_2N,H), (HO,H), (F,H), (HCC,H), (NC,H).

lation shown in eq 4, from which the ion-molecule clusters have been eliminated.

$$\Delta E^b_{X,Y} \simeq \tfrac{1}{2}[\Delta E^b_{X,X} + \Delta E^b_{Y,Y}] + \tfrac{1}{2}\Delta E^\circ + \{(\Delta E^\circ)^2/8[\Delta E^\ddagger_{X,X} + \Delta E^\ddagger_{Y,Y}]\} \quad (4)$$

Figure 4 compares $\Delta E^b_{X,Y}$, calculated from the energy difference between the reactants and **2**, with the values predicted by eq 4. Although the standard deviation of these results shows slightly more scatter ($\sigma_N = 1.4$ kcal/mol) than the correlations of Figure 3, it seems clear that eq 4 is a useful rate-equilibrium relationship.[13]

A number of conclusions can therefore be stated: (1) the Marcus equation and its variants are of paramount importance for the treatment of rate-equilibrium data; (2) consequently, the concepts of nucleophilicity and leaving group ability become merged and absorbed into the intrinsic barriers and heats of reaction;[8,9] (3) a treatment of S_N2 reactivity is thereby provided which is freed from the limitations of frontier molecular orbital theory;[14] (4) the gas-phase S_N2 behavior of HOO^- is entirely normal, as can be seen in Figures 3 and 4, as well as Figures 2 and 3 of ref. 4. The implications of these findings for interpretations of the α effect[15] will be discussed elsewhere.

Acknowledgment. This research has been supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund, administered by the American Chemical Society. We gratefully thank the Advisory Research Committee of Queen's University and Wayne State University for generous allocation of computing funds.

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[13] It is hoped that quantitative comparisons of computed $\Delta E^b_{X,Y}$ values with experiment will become feasible with basis sets that afford quantitative agreement with experimental heats of reaction and intrinsic barriers. See footnote 17 of ref 4.

[14] Wolfe, S.; Kost, D. *Nouv. J. Chim.* **1978**, *2*, 441-443 and references cited.

[15] Wolfe, S.; Mitchell, D. J.; Schlegel, H. B.; Minot, C.; Eisenstein, O. *Tetrahedron Lett.*, in press.

Nucleophilic Activation of CO for Reduction by Hydrogen

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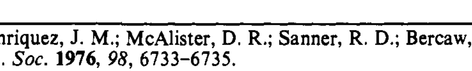
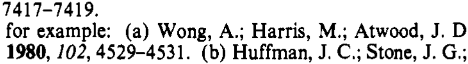
The production of chemicals from carbon monoxide and hydrogen feedstocks is a matter of intense current interest and vigorous investigation. Homogeneous transition-metal catalysts for this conversion are especially attractive, as they appear to offer promise of the selectivity and mechanistic simplicity which heterogeneous catalysts traditionally lack. Though the homogeneous hydrogenation of carbon monoxide has only recently been achieved,[1,2] the literature of the past few years abounds with reports of such reactions. The activation of carbon monoxide toward such homogeneous reduction by hydrogen has been approached in three ways: coordination of carbon monoxide to soluble transition-metal clusters,[3] coordination of Lewis acids to the oxygen atom of transition-metal bound carbon monoxide,[2,4] and either inter- or intramolecular donation of hydride to the carbonyl carbon atom.[5] We now wish to propose a new method of carbon monoxide activation toward homogeneous reduction and present experimental evidence demonstrating the utility of this approach in the production of functionalized organic products.

Fischer's pioneering work on the generation and isolation of transition-metal-carbene complexes,[6] coupled with Casey's report of the hydrogenation of such a complex[7] (reaction 1), suggested that attack at carbonyl carbon by an external nucleophile could provide the activation of carbon monoxide required for reduction in the manner presented in reactions 2-7. This cocatalyst scheme



$$(CO)_5Cr{=}C(OCH_3)(C_6H_5) \xrightarrow[140\ ^\circ C,\ THF]{1.8\ atm\ H_2} C_6H_5CH_2OCH_3 \quad (1)$$



$$M(CO)_x + {:}Nuc^- \rightleftharpoons (CO)_{x-1}M{=}C(O^-)(Nuc) \quad (2)$$

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[1] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733-6735.

[2] Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796-2797.

[3] See, for example: (a) Muetterties, E. L. *Science* (*Washington, D.C.*) **1977**, *196*, 839-848. (b) Thomas, M. G.; Beier, B. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 1296-1297. (c) Whitmire, K.; Shriver, D. F. *Ibid.* **1980**, *102*, 1456-1457. (d) Bradley, J. S.; Ansell, G. B.; Hill, E. W. *Ibid.* **1979**, *101*, 7417-7419.

[4] See, for example: (a) Wong, A.; Harris, M.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 4529-4531. (b) Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *Ibid.* **1977**, *99*, 5829-5831. (c) Lapidus, A. L.; Savel'ev, M. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 335-338; *Chem. Abstr.* **1980**, *93*, 7585y.

[5] See, for example: (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121-129. (b) Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244-7246. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927-1933. For closely related work, see: Tam, W.; Wong, W.-K.; Gladysz, J. A. *Ibid.* **1979**, *101* 1589-1591. (d) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1979**, *182*, C57-C60. (e) Wong, K. S.; Labinger, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3652-3653. (f) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *199*, C9-C12.

[6] For reviews, see: (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1-32. (b) Connor, J. A. *Organomet. Chem.* **1976**, *5*, 245-258. (c) Cotton, F. A.; Lukehart, C. M. *Prog. Inorg. Chem.* **1972**, *16*, 487-613. (d) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545-574. (e) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691-1694.

[7] Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 1651-1652.

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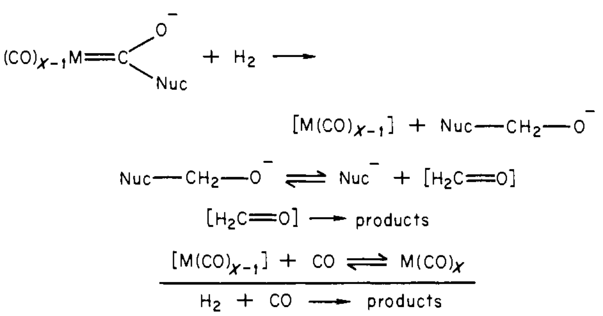
Table I. Stoichiometric Transition-Metal–Carbene Complex Hydrogenations[a]

metal carbonyl	solvent	temp, °C	product yields, % DMF	Me_3N	other
$Cr(CO)_6$	THF	130	30		CH_3OH (10%)
$Cr(^{13}CO)_6$	THF	130	*b*		$^{13}CH_3OH$
$Cr(CO)_6$	HMPA	130	15	5	
$Cr(CO)_6$	HMPA[c]	130	23	3	
$Cr(CO)_6$	HMPA[d]	130	*b*		Me_3N-d_3
$Cr(CO)_6$	HMPA	70	40		
$Cr(CO)_6$	HMPA/DMA[e]	130	*b*	*b*	Me_2NEt
$Cr(^{13}CO)_6$	HMPA	130	*b*		Me_3N-$^{13}C_1$
$(CO)_5Cr{=}C(OLi)NMe_2$[f]	HMPA	130	35	5	
$Mo(CO)_6$	HMPA	130	17	trace	
$W(CO)_6$	HMPA	130	18		
$Mn_2(CO)_{10}$	HMPA	130		2	
$Re_2(CO)_{10}$	HMPA	130	10	2	
$Fe(CO)_5$	HMPA	130	8	8	

[a] Except as noted, all reactions run with ~3.5 mmol of metal carbonyl and an equimolar amount of $LiNMe_2$ in 5 mL of solvent under 35 psi H_2 for 24 h. [b] Product present; yield not determined. [c] 75 psi H_2. [d] 35 psi D_2. [e] DMA = *N,N*-dimethylacetamide. [f] No added $LiNMe_2$; complex synthesized by the method of Fischer et al.[10a]



$$(CO)_{x-1}M{=}C(O^-)(Nuc) + H_2 \longrightarrow [M(CO)_{x-1}] + Nuc{-}CH_2{-}O^- \qquad (3)$$

$$Nuc{-}CH_2{-}O^- \rightleftharpoons Nuc^- + [H_2C{=}O] \qquad (4)$$

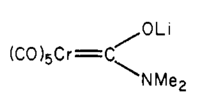
$$[H_2C{=}O] \longrightarrow \text{products} \qquad (5)$$

$$[M(CO)_{x-1}] + CO \rightleftharpoons M(CO)_x \qquad (6)$$

$$H_2 + CO \longrightarrow \text{products} \qquad (7)$$

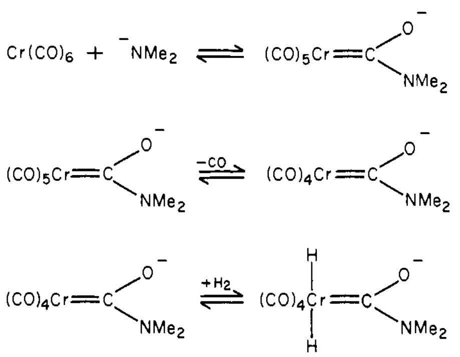
is particularly attractive since it should lead directly to functionalized products, is mechanistically analogous to proposed water-gas shift schemes,[8] and may play a role in heterogeneous systems which do not dissociate CO on adsorption.[9] We have carried out a series of model stoichiometric reactions designed to explore the potential of this proposed scheme and present the results of this investigation below.

Fischer has shown[10] that anionic carbene complexes are readily generated from a variety of metal carbonyls when they are treated with lithium dialkylamides. The hydrogenation of a 1:1 mixture of chromium hexacarbonyl and lithium dimethylamide ($LiNMe_2$), known[10] to produce



1

in tetrahydrofuran[11] (35 psi H_2, 130 °C, 18–24 h) yielded several organic products, including methanol (10% yield) and dimethylformamide (DMF, 30% yield). When carbon-13 enriched[12] $Cr(CO)_6$ was used, the methanol obtained was similarly enriched, confirming that the carbon source was indeed carbon monoxide. Dark solids gradually precipitated during the course of this hydrogenation, however, so the source of the observed organic products, whether homogeneous or heterogeneous, is unknown. When hexamethylphosphoric triamide (HMPA) was used as the solvent for the hydrogenation, no solids were precipitated; the reaction mixture remained homogeneous. Though only traces of methanol were observed in this reaction, DMF was formed, in somewhat lower yield than in THF (15%). The low yield of DMF obtained appears to be due to problems with the formation and thermal stability of the anionic carbene complex **1**; if the reaction is run with preformed carbene complex, the DMF yield is increased to 35%, while if the reaction is run at 70 °C instead of 130 °C, a 40% yield of DMF is obtained. A reasonable mechanism[13] for DMF formation is suggested in reactions 8–11. Prior carbon



$$Cr(CO)_6 + {}^-NMe_2 \rightleftharpoons (CO)_5Cr{=}C(O^-)NMe_2 \qquad (8)$$

$$(CO)_5Cr{=}C(O^-)NMe_2 \overset{-CO}{\rightleftharpoons} (CO)_4Cr{=}C(O^-)NMe_2 \qquad (9)$$

$$(CO)_4Cr{=}C(O^-)NMe_2 \overset{+H_2}{\rightleftharpoons} (CO)_4Cr(H)_2{=}C(O^-)NMe_2 \qquad (10)$$

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(8) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4688–4694.

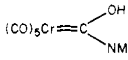
(9) Ichikawa has proposed interactions between surface hydroxy groups of basic oxide supports and chemisorbed CO: Ichikawa, M. International Seminar on the Relationship Between Metal Cluster Compounds, Surface Science, and Catalysis, Pacific Grove, CA, 1979.

(10) (a) Fischer, E. O.; Winkler, E.; Kreiter, C. G.; Huttner, G.; Kreig, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 922–924. (b) Fischer, E. O.; Kollmeier, H. J. Ibid. **1970**, *9*, 309–310.

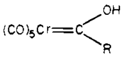
(11) In a representative reaction, a glass pressure vessel was charged with 0.75 g of $Cr(CO)_6$ (3.4 mmol), 0.175 g of $LiNMe_2$ (3.4 mmol), and 5 mL of HMPA (vacuum distilled from CaH_2 and then from Na metal; stored under N_2) or 5 mL of THF (distilled from benzophenone ketyl) in an inert atmosphere box. The vessel was sealed to a pressure head bearing an inlet valve, a pressure gauge, and a septum-capped ball valve. The apparatus was connected to a hydrogen line and repeatedly filled to 35 psi of H_2 and then vented. Finally, the apparatus was pressured to 35 psi of H_2, and the lower part was immersed in a silicone oil bath of the desired temperature. Vapors were periodically sampled by gas-tight syringe through the septum. Products were analyzed by analytical gas chromatography (GC) and/or GC mass spectrometry (GC/MS). Vapors were analyzed for CH_3OH on a 10-ft Porapak Q column at 110 °C, flow rate 60 mL/min, and for amines on a 6-ft Carbopack B/4% Carbowax 20 M/0.8% KOH column at 70 °C, flow rate 20 mL/min. Solutions were analyzed on the Porapak Q column and on a 10-ft 10% Versamid 900 on Chromosorb Q column at 70 °C, flow rate 40 mL/min (for DMF). GC/MS analyses were performed on a Kratos instrument by using a 10-ft Porapak Q column at 110°C.

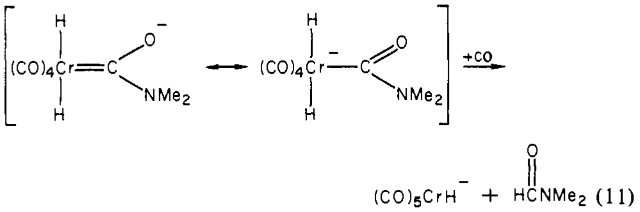
(12) Carbon-13 enriched $Cr(CO)_6$ was prepared by heating $Cr(CO)_6$ in THF at 130 °C under 35 psi ^{13}CO (Monsanto Mound) for 4 days and then filtering off the crystalline material which precipitated upon cooling.

(13) Protonation of the anionic complex **1** with trifluoroacetic acid in acetone-d_6 at 25 and 130 °C does not give rise to DMF, ruling out formation of



followed by its thermal decomposition to give DMF, in contrast to the reactivity of




(11)

monoxide dissociation (reaction 9) is proposed in accord with Casey's observations.[7] The carbene complex is redrawn as an anionic carbamoyl complex in reaction 11 to show more clearly the postulated reductive elimination step. Several other binary transition-metal carbonyl complexes were investigated under analogous conditions; the results are presented in Table I. Though the activating nucleophile (NMe_2^-) is incorporated in the product (DMF) of the above reactions, precluding catalytic operation, the results nevertheless suggest that nucleophilic attack at transition-metal-bound carbon monoxide can indeed provide the activation required for reduction by molecular hydrogen under exceptionally mild conditions.

Several of the stoichiometric systems using HMPA as solvent were observed[14] to generate trimethylamine (Me_3N) in addition to DMF (see Table I). Though the yields of Me_3N were quite low (2–8%), several significant observations with regards to its formation in the $Cr(CO)_6/LiNMe_2$ reaction were made. If the reaction was run under deuterium (D_2) instead of hydrogen, the Me_3N product displayed a mass spectrum consistent with Me_3N-d_3, while if carbon-13 enriched $Cr(CO)_6$ was used, the Me_3N was similarly enriched. Hydrogenation at 70 °C instead of 130 °C gave no Me_3N, though DMF was still formed. Finally, hydrogenation in the presence of *N,N*-dimethylacetamide gave rise to both Me_3N and dimethylethylamine. Apparently, then, Me_3N arises from further reduction of the primary product DMF. Given the mechanistic scheme suggested in reactions 8–11, it seems likely that the active hydrogenation agent is the $(CO)_5CrH^-$ anion.[15] Indeed, we have found that $\{[(C_6H_5)_3P]_2N\}^+$-$[(CO)_5CrH]^-$ quantitatively reduces several amides (DMF, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide) to the corresponding tertiary amines (Me_3N, dimethylethylamine, and triethylamine, respectively) when stirred with an excess of the amide in HMPA solvent at 130 °C under 35 psi of hydrogen (the same conditions used for the carbene hydrogenations). These are exceptionally mild conditions for a transition-metal mediated reduction of an amide, and studies to elucidate the mechanism of this reduction are currently in progress. The fact that $(CO)_5CrH^-$ can indeed reduce DMF to Me_3N gives credence to the proposed mechanism for DMF (and Me_3N) formation,[16] though the reasons for the low yields of Me_3N obtained are unknown. The NMe_2^- unaccounted for as DMF and Me_3N appears to be present as a metal complex (with either lithium or chromium; dimethylamine is produced upon hydrolysis), and perhaps this in some way interferes with the hydrogenation step.[17]

Homogeneous systems have been found, then, which are able to convert transition-metal-bound carbon monoxide to a formyl group (in DMF) and a methyl group (in Me_3N) once it is activated by nucleophilic attack. Though the activating nucleophile is incorporated in the products observed, the results suggest the validity of this approach to carbon monoxide activation and reduction. Obvious extensions of these reactions to other metals and nucleophiles are being vigorously pursued.

Acknowledgment. This work was supported by the Department of Energy. K.M.D. thanks the Fannie and John Hertz Foundation for fellowship support.

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[14] Furthermore, the group 6 metals [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$] appeared to produce small amounts of lower hydrocarbons [CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, 1-C_4H_8, and *n*-C_4H_{10}]. Yields were extremely low, however (typically 0.1–1.0%, based on carbonyl), precluding the labeling studies essential to a critical evaluation of these observations.

[15] The synthesis and characterization of this hydride anion has just appeared in print: Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644–1646. We prepared the bis(triphenylphosphine)iminium salt of this anion in an analogous fashion and are grateful to M. Darensbourg and J. Deaton for supplying us with a preprint of this publication.

[16] The active hydrogenation agent is not necessarily $(CO)_5CrH^-$; in HMPA at 130 °C, this complex may be converted to other species [e.g., $Cr_2(CO)_{10}H^-$] as well as exchange HMPA for CO ligands. As the model studies using preformed $[(CO)_5CrH]^-PPN^+$ show, however, either it or whatever species to which it may be converted is quite active as a hydrogenation agent.

[17] A referee questioned whether reaction of $LiNMe_2$ with H_2, a potential hydride source,[18] could provide an alternate mechanism for CO or DMF reduction in the hydrogenation systems. Control experiments preclude this possibility: (1) a mixture of $LiNMe_2$ and DMF in HMPA under the usual hydrogenation conditions produces no Me_3N; (2) addition of 1 equiv of LiH to the $Cr(CO)_6/LiNMe_2$ system in HMPA does not enhance DMF or Me_3N formation.

[18] Dirian, G.; Botter, F.; Ravoire, J.; Grandcollot, P. *J. Chim. Phys.* **1963**, *60*, 139–147.

Book Reviews

Quantitative Analysis. Fourth Edition. By R. A. Day, Jr., and A. L. Underwood (Emory University). Prentice Hall, Inc., Engelwood Cliffs, N. J. 1980. xi + 660 pp. $12.50.

This particular text has been widely used and survived three editions and field trials with both major and nonmajor chemistry courses. Basically, this text can be used readily by students who have had a course in general chemistry and elementary algebra. The 4th edition has been improved with regard to presentation of classical material such as titrimetric methods, concepts of stoichiometry, and gravimetric methods and separations. The authors also present a more than adequate presentation on errors and the treatment of analytical data. Topics such as propagation of error and test of significance of the result are included and are of value to any scientific field based on measurements.

The organization of chapters appears to be logical and follows a logical sequence of laboratory and classroom presentations, with the exception that the principles of mass measurement and associated problems with the ultimate accuracy of this fundamental measurement are relegated to the experimental part. Yet, historically, the measurement of mass is practically the backbone of analytical chemistry and should be presented following the analysis of error. The practical weighing procedure, the different types of balances, and care of the balances could be left in chapters dealing with laboratory techniques in the back of the book, as is.

This text presents quite an extended treatment on separations. In fact, three chapters are dedicated to liquid-liquid extraction, gas-liquid chromatography, and liquid chromatography. It is noteworthy that in these chapters the authors develop a suitable theoretical base which can be easily assimilated by the average student. Concepts such as multiple extraction, Craig-pseudocountercurrent extraction, and binomial distribution are clearly presented and are not overburdened by advanced material. In addition, concepts dealing with the height equivalent of theoretical plates, HETP, in gas chromatography and the importance of the van Deemter equation are presented clearly. Furthermore, the discussion of the separation factors affecting separation efficiency and detectors is treated adequately at the beginners's level.

In Chapter 5 and 6 the authors state that the pH = $-\log [H_3O^+]$ and they use the example that the pH for a solution having $[H_3O^+] = 0.1$ is equal to 1. This would be in agreement with the original concept proposed by Sørensen stating that pH = $-\log C_{H^+}$. However, the presently accepted definition for pH as modified by Sørensen and Lindstrøm-Lang is based on the activity of hydrogen or hydronium ions rather than on concentrations. It is true that the differences are negligible in dilute