JOURNAL OF CATALYSIS 54, 98–101 (1978)

On the Interpretation of Apparent Heats of Adsorption from Kinetics for a Nonuniform Surface

In a study of the disproportionation of propylene on cobalt–molybdate catalysts, Moffat and Clark (*1*) demonstrated the existence of reversible rate temperature maxima. At temperatures below $T_{\max}$, the rate was found to be represented by the Langmuir–Hinshelwood equation,

$$r = (kK^2p^2)/(1 + Kp)^2. \qquad (1)$$

For a uniform surface it was shown that a rate temperature maximum would occur if $q > E/2$. A similar constraint was presented by Maatman *et al.* (*2*). However, when the rate and equilibrium constraints were extracted from Eq. (1), it was found that E = 8.2 kcal/mole and q = 2.8 kcal/mole. These values violated the constraint given above, and the authors demonstrated qualitatively that a rate temperature maximum and a low heat of adsorption could be reconciled in terms of a nonuniform surface with a distribution of site energies. We wish to present here some calculations that quantify these arguments and to illustrate that kinetic parameters obtained from an analysis of the rate equation can be a sensitive function of the surface nonuniformity. On a nonuniform surface, the rate would be represented by

$$r = \sum_{i=1}^{N} k_i \frac{K_i^2p^2}{(1 + K_ip)^2} \qquad (2a)$$

for discrete sites or by

$$r = \int_{q_1}^{q} k_q \frac{K_q^2p^2}{(1 + K_qp)^2} n_q dq \qquad (2b)$$

for a continuous distribution of adsorption site energies. If Eq. (2a) is compared with Eq. (1) for the case in which k_i is constant ($= k'$), the experimental or apparent rate and equilibrium constants are given by

$$K = (1/p)[(F/H) - 1] \qquad (3a)$$

and

$$k = \frac{k'p^2F^3}{(F - H)^2}, \qquad (3b)$$

where

$$F = \sum_{i=1}^{N} \frac{K_i^2}{(1 + K_ip)^2} \qquad (4a)$$

and

$$H = \sum_{i=1}^{N} \frac{K_i^2}{(1 + K_ip)^3}. \qquad (4b)$$

Analogous expressions for K and k can

TABLE 1

Apparent Heat of Adsorption Calculated by a Least-Squares Fit of ln K vs $1/T$ at Different Temperatures

Temperature range (K)	q' (kcal/mole)	
	Discrete distribution	Continuous distribution
200–300	7.94	8.43
250–350	7.26	8.23
300–400	5.13	7.31
350–450	3.06	5.93
400–500	4.06	5.65
450–550	6.38	6.85
500–600	8.57	8.51
550–650	10.56	9.83
600–700	11.34	10.74

0021-9517/78/0541-0098$02.00/0

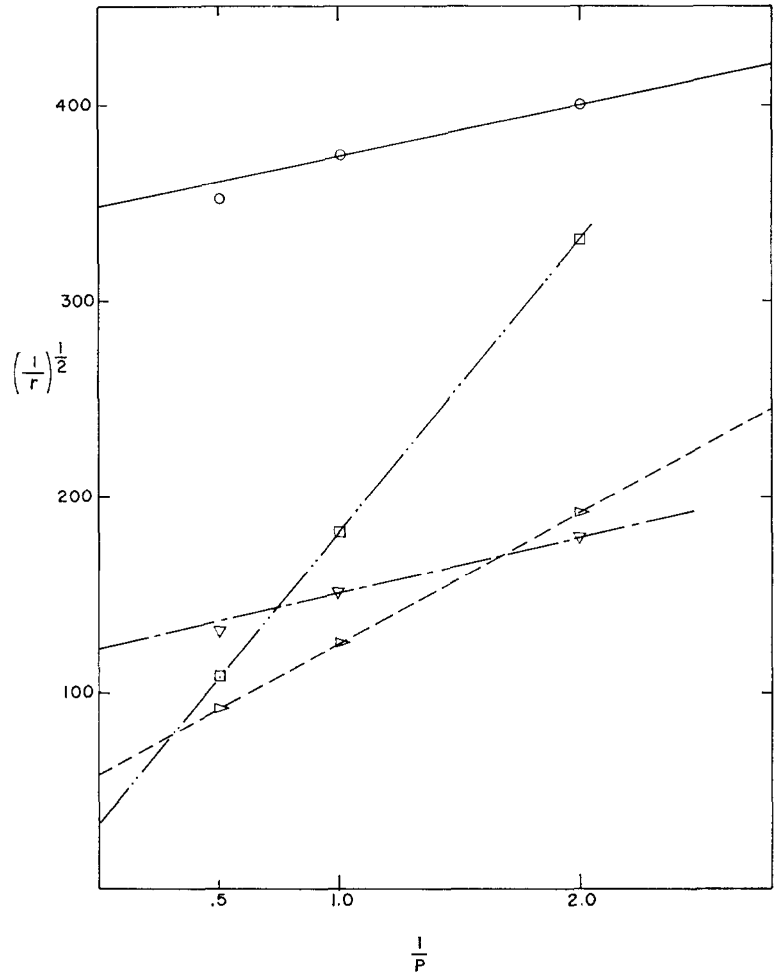

FIG. 1. Langmuir–Hinshelwood correlation of the rate for a discrete system at 400 (○), 500 (▽), 600 (△), and 700 K (□).

also be obtained for the case of a continuous distribution of surface sites. The apparent heat of adsorption can be obtained experimentally from the adsorption equilibrium constant,

$$q = R\frac{\partial \ln K}{\partial(1/T)}. \tag{5}$$

We have made calculations by assuming three equally probable types of discrete sites with $q_i = 8$, 10, and 12 kcal/mole ($i = 1, 2, 3$) and for a continuous distribution of sites between 8 ($= q_1$) and 12 ($= q_2$) kcal/mole where n_q is constant. The activation energy was taken to be constant at 10 kcal/mole and the adsorption entropy was taken to be -20 e.u. The spread in adsorption heats is, therefore, relatively small and each site individually satisfies the condition giving a rate temperature maximum (i.e., $q_i > E/2$). Figure 1 shows that, for a discrete system of sites, the rate would still be represented by a bimolecular Langmuir–Hinshelwood equation with rate temperature maxima as shown in Fig. 2. The results for the continuous distribution of sites were similar. Over the temperature range of 400–700 K the apparent activation energies were found to be 8.54 and 8.42 kcal/mole for the discrete and continuous distributions, respectively. Since each site was assumed to have the same E_i, the weighted average is only slightly different from the true value. By contrast, there is a significant variation in the apparent heat of adsorption with temperature. Table 1 gives the apparent heat of adsorption calculated from a least-squares fit of $\ln K$ vs $1/T$ in different temperature increments, and Fig. 3 gives q' calculated directly from Eqs. (3a) and (5). The apparent heat approaches the lower limit (i.e., 8 kcal/mole) at low temperatures and the upper limit (i.e., 12 kcal/mole) at high temperatures. In the intermediate temperature range, the apparent heat of adsorption can fall to 2–3 kcal/mole. If the calculations are repeated with site energies of 8, 12, and 16 kcal, the *apparent* heat of adsorption can become negative.

Thus, a relatively small distribution of site energies (i.e., $\Delta q = 4$–8 kcal/mole) can have a profound effect on the apparent heat of adsorption. Even though the reaction exhibits a rate temperature maximum, the apparent heat of adsorption can be significantly less than $E/2$. In a study of the initial rates for the dis-

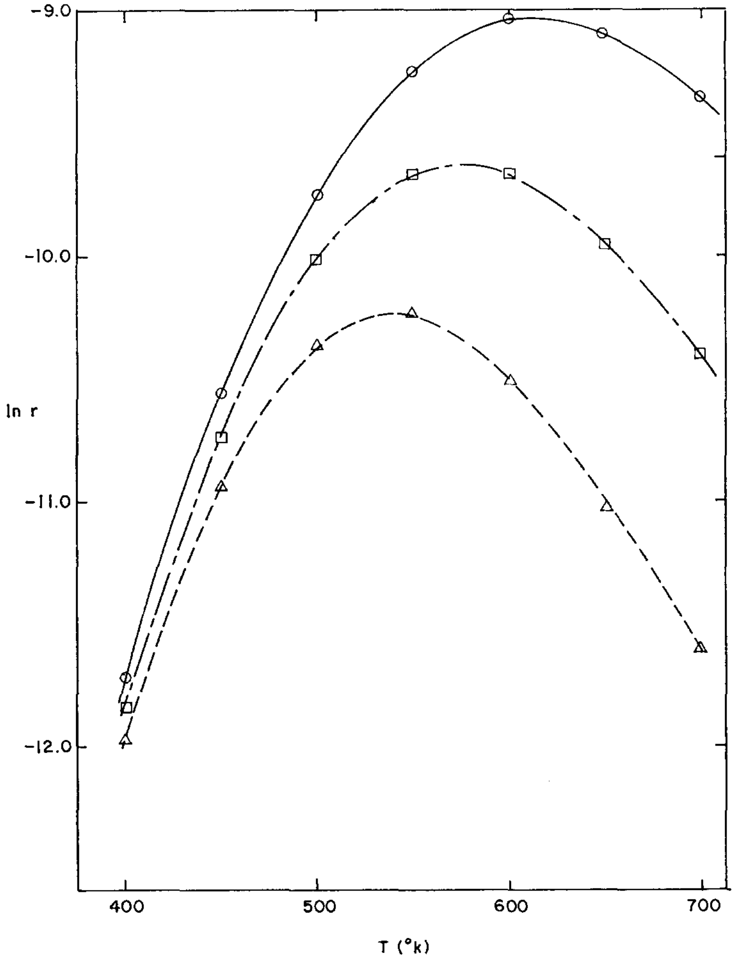

FIG. 2. Rate temperature maxima for a discrete system of adsorption sites at 0.5 (△), 1.0 (□), and 2.0 atm (○).

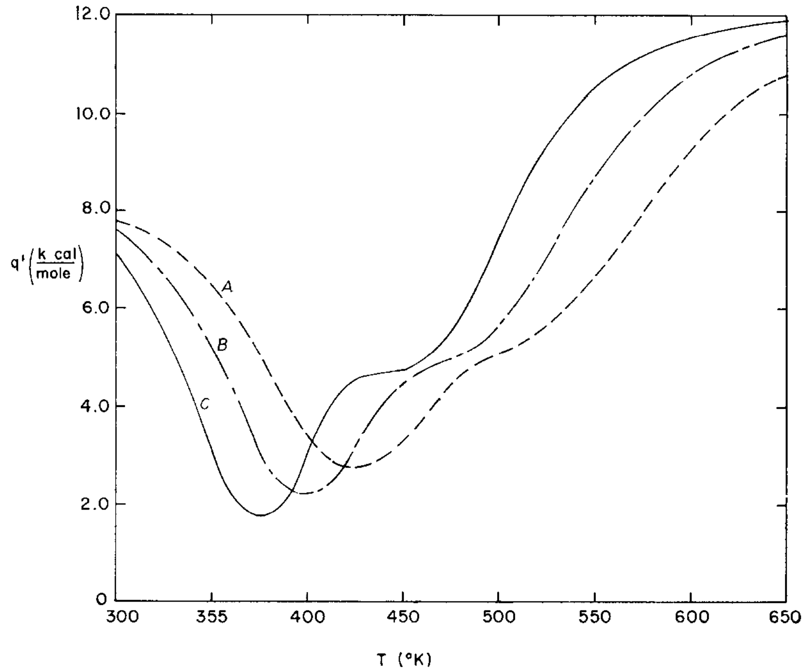

Fig. 3. Apparent heat of adsorption as a function of temperature for 2.0 (A), 1.0 (B), and 0.5 atm (C) with q_i = 8, 10, and 12 kcal/mole.

proportionation of propylene on WO_3/SiO_2, Luckner *et al.* (*3*) found that the results were represented by a bimolecular Langmuir–Hinshelwood equation, but that the apparent heat of adsorption was −4.55 kcal/mole. Since it is unlikely that the adsorption of propylene on WO_3 would be endothermic, a more plausible interpretation, in view of the calculations given above, is that the reaction occurs on a nonuniform surface with low heats of adsorption that could, depending upon the distribution, give a negative apparent heat of adsorption.

The need for caution in interpreting heats of adsorption (*4*) and adsorption entropies (*5*) from kinetic data has already been emphasized. The calculations considered here illustrate that even a small variation in the distribution of adsorption heats can significantly alter the apparent heat of adsorption, which can be less than the smallest actual value and, with a slightly broader distribution, can even become negative.

REFERENCES

1. Moffat, A. J., and Clark, A., *J. Catal.* **17**, 264 (1970).
2. Maatman, R. W., Leenstra, D. L., Leenstra, A., Blandespoor, R. L., and Rubingh, D. N., *J. Catal.* **7**, 1 (1967).
3. Luckner, R. C., McConchie, G. E., and Wills, G. B., *J. Catal.* **28**, 63 (1973).
4. Carberry, J. J., *Nature* (*London*) **189**, 391 (1961).
5. Boudart, M., Mears, D. E., and Vannice, M. A., *Ind. Chim. Belg.* **32**, 28 (1967).

A. W. Aldag
A. Clark

School of Chemical Engineering and Materials Science
University of Oklahoma
Norman, Oklahoma 73019

Received June 6, 1977; revised March 9, 1978