suggest solvent interaction with the hyperconjugated methyl group to counterbalance the small augmenting influence on the carbonyl moment. The data, however, are insufficient for any definite indication.

Further work is planned to investigate hyperconjugation and preferred configurations in unsaturated methyl ketones, and some analogous aldehydes.

LUBBOCK, TEXAS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON, N. J., AND DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Kinetics of Active Centers in Surface-catalyzed Reactions

BY NATHANIEL THON AND H. AUSTIN TAYLOR

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Discrepancies between initial rate and course of reaction kinetic laws in heterogeneously catalyzed reactions are interpreted by the rate-determining role of the surface density of active centers which are dissociatively chemisorbed particles of only one reactant. Surface-catalyzed reactions involve an opening step consisting in a reaction between the active centers at the surface and gaseous molecules of the other reactant. Except in simplest cases, this step will in general have to be followed by further reactions with gaseous molecules to form the final products. The rate-determining active-center density at the surface can be maintained over the course of the reaction through a chain mechanism, bringing forth the product and regenerating the active centers. On the other hand, the active-center density can be subject to decay and decrease with increasing degree of conversion according to Elovich's exponential law, previously found widely applicable to chemisorption. The limiting case of $\alpha \approx 0$ corresponds to absence of such active-center decay. The rate of the opening step is determined by the density of the active centers produced by one reactant and the gas-phase concentration of the other reactant.

1. Initial Rate and Course of Reaction Kinetics.—In contrast to homogeneous reactions which as a rule obey the same kinetic law both with respect to the initial rates measured in different runs (with different reactant compositions at the start) and over the course of each single run, the kinetics of surface-catalyzed reactions are different depending on whether they refer to initial (or near initial) rates or to the course of the reaction. Experimental material sufficient to provide for the *same* reaction *both* the law of the variation of the initial rates as a function of the varied initial reactant concentrations *and* the law of the variation of the rate with the progress of the reaction, is much less abundant than data giving merely *either* the near initial rate law (or a mean rate law over a definite over-all range of conversion) *or* the course of reaction law. Still, in a number of instances where the available data permit a comparison, the initial and the course law turn out to be inconsistent. A mere statement of an "order" without specifying whether it refers to near initial rates or to the course of the reaction, is indefinite and may be seriously misleading; one cannot, in heterogeneously catalyzed reactions, derive "the" order of the reaction, indifferently and interchangeably, either by comparing the initial rates of separate runs or by following the progress of the reaction in one run, as, since van't Hoff's days, is commonly and legitimately done in homogeneous systems.

As examples of this inconsistency, we may quote Pease's[1] work on the hydrogenation $C_2H_4 + H_2 \rightarrow C_2H_6$ on Cu. At 0° and at 200°, the initial rates are described, respectively, by the kinetic laws $[H_2]^{0.6}[C_2H_4]^{-0.4}$ and $[H_2]^{0.8}[C_2H_4]^{0.66}$. Neither of these laws applies to the course of the reaction (over the extent of conversion covered in the original work) at the corresponding temperature. It is evident that the progress of the reaction follows some entirely different law; we shall come back to it further below under 5. Another example is the $NH_3 + D_2$ exchange on Fe, studied by Farkas.[2] The near initial rates, from one run to another, are, roughly, of 0.5 order in D_2, and zero order in NH_3. However, this square-root law fails when one tries to apply it to the course of the reaction. In the six representative experiments, with different and varied initial proportions of D_2 and NH_3, plotted in Figs. 3 and 4 (ref. 2, p. 419), and which bear out the $[D_2]^{0.5}[NH_3]^0$ law for the initial rates, the rates over the whole course of the exchange are remarkably constant and show no decrease such as would have to be expected if the $[D_2]^{0.5}$ mass action law were to govern the course of the conversion. The course of the reaction is very nearly zero order throughout.

2. Active Centers in Surface Catalysis.—The root of this discrepancy lies in the rate-determining role of the catalyst surface. We postulate that the rate at each stage is proportional to the surface density *of active centers*. By that term, we mean dissociatively chemisorbed particles of *one*, and only one, reactant of the system. The question of which of the reactants provides the active centers, must be answered specifically in each case in the light of the factual, especially the kinetic evidence. Without at this point engaging in detailed analysis, we shall specify that in hydrogenation reactions, it is plausible to identify the active centers as chemisorbed hydrogen atoms, H(ads). In oxidations it is chemisorbed oxygen,[3] in saturated hydrocarbon reactions a chemisorbed alkyl, in ammonia synthesis most probably N(ads). In catalyzed reactions between CO and H_2 which produce mainly CH_4 and H_2O, it appears plausible to identify the active centers with H(ads), whereas in the Fischer–Tropsch process, which produces C–C bonds, active centers are dissociatively chemi-

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[1] R. N. Pease, THIS JOURNAL, **45**, 1196, 2235 (1923).

[2] A. Farkas, *Trans. Faraday Soc.*, **32**, 416 (1936).

[3] We see no basis yet for deciding whether the oxygen is chemisorbed in the form of atoms, or as a molecule; the latter would amount to a chemisorbed peroxide center.

sorbed CO. The reactant which, in each case, forms the active centers, is to be termed the center-making reactant.

This postulate of only one kind of active centers being responsible for each given catalytic reaction is opposed to the generally adopted scheme of catalytic reactions wherein all reactants are obligatorily adsorbed at the surface. The possibility of reactions between one adsorbed and one gaseous reactant may have been hinted at sporadically in specific instances, but was never followed through to a conclusion, and never elevated to anything like a general scheme. A mechanism put forward by Rideal[4] wherein chemisorbed species are assumed to react with molecules, van der Waals adsorbed in gaps in the chemisorbed layer, is fraught with difficulties and has gained no favor. The overwhelmingly accepted scheme at the present time is that of reactions between adsorbed reactants; to it we oppose, as a matter of *general* principle, chemisorptive activation of only one species, followed by a reaction with an unadsorbed species. It is logically consistent with the fundamental pattern of all chemical reactions which involve one activated and one inert partner.

3. Production of Active Centers.—In general, active centers will be produced on first contact with the gaseous center-making reactant. Following a mostly very short formative stage, a near initial stationary active center density n_0 will be established which, by a reasoning entirely analogous to that applied to the initial site density for chemisorption[5] must be proportional to a *positive* power of the concentration of the center-making reactant, less than or at most equal to unity. This initial center density can be depressed by competition on the part of a second reactant acting as a center-unmaker; in that case, the empirical initial rate law may involve this second reactant to a negative power, generally fractional. Instances of such inhibitions by one reactant, with respect to initial rates, are numerous: as examples, the $CH_4 + D_2$ exchange on Ni is inhibited by excess D_2 (Kemball[6]); the initial rate of the $NH_3 + D_2$ exchange, under the conditions of Weber and Laidler[7]), is inhibited by excess NH_3; the reaction $CO + H_2 \rightarrow CH_4, H_2O$ studied by Jungers, *et al.*,[8] is inhibited by an initial excess of CO. Our own interpretation of the empirical functional dependence of the initial rate on the initial concentration of the center-unmaking species will be given further below in part 6.

4. Maintenance of the Active Center Density through Chains.—Insofar as the rate of reaction is proportional to the active center density, its variation over the course of the process will be governed by the variation of that density. In our paper on the kinetics of chemisorption[5] we were led to the conclusion that, while the initial site density is an algebraic function of the initial concentration of the gas, its further fate with the progress of the process follows laws of its own and does not any further follow the changing mass action of the gas. In complete analogy with it, the once established active center density in a catalytic reaction need not follow the changing mass actions of the reactants. The surface density of active centers can be maintained if their consumption by the reaction is compensated by regeneration through a *chain mechanism.*

The simplest example of such a chain mechanism is the $H_2 + D_2$ exchange. Active centers are, indifferently, H(ads) or D(ads). The reaction schemes are

$$\mathrm{H(ads)} + \mathrm{D_2(gas)} \longrightarrow \mathrm{HD(gas)} + \mathrm{D(ads)}$$
$$\mathrm{D(ads)} + \mathrm{H_2(gas)} \longrightarrow \mathrm{HD(gas)} + \mathrm{H(ads)}$$

producing HD and giving back the original H(ads), and

$$\mathrm{D(ads)} + \mathrm{H_2(gas)} \longrightarrow \mathrm{HD(gas)} + \mathrm{H(ads)}$$
$$\mathrm{H(ads)} + \mathrm{D_2(gas)} \longrightarrow \mathrm{HD(gas)} + \mathrm{D(ads)}$$

giving back the original D(ads).

In this simplest instance, the first reaction between an active center and the gas, which we term the "opening step," brings forth directly the final product. This is not so in the following scheme for the hydrogenation $C_2H_4 + H_2 \rightarrow C_2H_6$. We take the active centers to be H(ads). These react with gaseous C_2H_4 in the opening step

$$\mathrm{H(ads)} + \mathrm{C_2H_4(gas)} \longrightarrow \mathrm{C_2H_5(ads)}$$

without as yet forming the product. This is produced in the next following step

$$\mathrm{C_2H_5(ads)} + \mathrm{H_2(gas)} \longrightarrow \mathrm{C_2H_6(gas)} + \mathrm{H(ads)}$$

which gives back the original active center H(ads). Thus, one and the same active center can produce a large number of product molecules, and the original center density can be maintained through chains.

In this scheme, desorption of reaction products is not unaccountably spontaneous, but is provoked by the impact of a gaseous molecule, and compensated by adsorption of another particle taking the place of the particle previously adsorbed at the same point. This scheme avoids the entirely improbable desorption of a product molecule through a judicious association of elementary fragments present at the surface.

Evidence for the existence of opening steps which do not in themselves bring forth the products is provided by such observations as those made by Elovich and Zhabrova[9] in consecutive, rather than simultaneous, admission of the reactants in the $C_2H_4 + H_2$ reaction on Ni. When H_2 was admitted first, allowed to be chemisorbed, the excess gas removed, and C_2H_4 admitted subsequently, no C_2H_6 was formed (or at least not enough to measure); but the reaction proceeded immediately, and at a rate undiminished as compared with that on virgin Ni, when both gases, $C_2H_4 + H_2$, were admitted. By our scheme, admission of C_2H_4 alone could produce only C_2H_5(ads), but no C_2H_6: this requires further reaction between C_2H_5(ads) and H_2(gas), *i.e.*, presence of *both* gaseous C_2H_4 and H_2. Another similar example is the observation of

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[4] E. K. Rideal, *Proc. Camb. Phil. Soc.*, **35**, 130 (1939).

[5] H. Austin Taylor and Nathaniel Thon, THIS JOURNAL, **74**, 4169 (1952).

[6] C. Kemball, *Proc. Roy. Soc. (London)*, **A207**, 539 (1951).

[7] G. Weber and K. J. Laidler, *J. Chem. Phys.*, **19**, 1089 (1951).

[8] J. Nicolai, M. D'Hont and J. C. Jungers, *Bull. soc. chim. Belge*, **55**, 160 (1946).

[9] S. Yu. Elovich and G. M. Zhabrova, *Zhur. fiz. Khim.*, **13**, 1761, 1776 (1939).

Garner, *et al.*,[10] that no CO_2 was produced when either CO alone was admitted to O_2, preadsorbed on Cu_2O, or O_2 alone to preadsorbed CO, but did appear in either case when both gases, $CO + O_2$, were admitted simultaneously.

5. Decay of Active Centers.—Maintenance of the active center density through regeneration by chains should give rise to zero-order kinetics throughout the course of the reaction, irrespective of the depletion of the gaseous reactants through conversion, barring of course severe exhaustion. Instances of zero-order *course* of catalytic reactions are known and will doubtless multiply on further analysis and investigation. On the other hand, and in analogy with the behavior of sites in chemisorption,[5] active centers in catalytic reactions should be subject to spontaneous decay caused by the very progress of the reaction. For chemisorption sites, we have postulated in our interpretation[5] of Elovich's law that the momentary site density is $n = n_0e^{-\alpha q}$, where q is the momentary extent of adsorption. In formal analogy thereto, the density n of *active centers* in reactions should vary with the momentary degree of conversion q according to the same law, $n = n_0e^{-\alpha q}$. The rate of reaction being proportional to n, it should decrease exponentially with increasing q, provided α is large enough for this decrease to be significant. The procedure of testing the applicability of this law has been described in our paper.[5]

In the work of Elovich and Zhabrova,[9] the course of the reaction $C_2H_4 + H_2 \rightarrow C_2H_6$ on Ni at 0° is shown to follow the rate law $dq/dt = ae^{-\alpha q}$ up to and over $q = 90\%$ conversion. The proof is given by linear graphs of q as a function of $\log (t_0 + t)$, where $t_0 = 1/a\alpha$, and a is the initial rate. The initial rate a is, in agreement with other work, nearly proportional to the initial $[H_2]$, and from zero to a small negative order in $[C_2H_4]$. The course of the same reaction on Cu, by the data of Pease,[1] quoted in part 1, can be described by the same law, with the values of the parameters given in Table I.

TABLE I

$C_2H_4 + H_2 \longrightarrow C_2H_6$ on Cu[1]

Temp., °C.	Initial pressure (atm.)	Initial, cc. H_2	Initial, cc. C_2H_4	t_0	$10^3\alpha$	a	q_{t_0}
0	1	26	26	40	5.7	4.1	..
	1	17.3	34.55	85	5.8	2.0	~3
	0.5	13.35	13.40	45	6.7	3.3	...
	0.5	8.65	17.35	85	7.4	1.5	~5
		$H_2:C_2H_4$					
200	1	1:1		0	11	13	
	1	2:1		0	12	12	
	1	1:2		0	12	10	

With respect to the amount q_{t_0}, the pressure decrease read at the abscissa t_0, and which must be deducted from the experimental q to bring the experimental initial rate in line with $a = 1/\alpha t_0$ from the plot, the manometric data permit no decision whether it corresponds to an initial massive adsorption or to some amount of initial abnormally fast reaction. On account of some deviation from linearity of two late readings in one run at 0° which may or may not be due to an experimental inaccuracy of these points, and which, if desired, can easily be made to disappear by altering the value of t_0, there is some uncertainty about the numerical values of the parameters. Still, it cannot be doubted that the exponential law represents as satisfactorily as can be the available data of the course of this reaction, and that no other rate law of the classic type, certainly not the initial rate law, does it.

Our interpretation of the Elovich law for chemisorption can be transposed into catalytic reaction, with "active center" substituted for "site." It means that when an active center reacts with a gaseous molecule, other centers not directly involved in the encounter may become inactivated; the rate of that inactivation of active centers, $-dn/dt$, is proportional to the product $\alpha n(dq/dt)$ of the momentary center density n and the momentary reaction rate dq/dt; the latter being proportional to n, it follows that $-dn/dt$ is proportional to αn^2, *i.e.*, the decay of active centers is a bimolecular process. The question of the nature of this bimolecular disappearance of active centers is obvious; the authors can offer no more specific answer to it at this time beyond the formal statement.

That active centers *do* decay over and above their actual consumption through reaction (in the absence of a regeneration by chains) follows from the work of Roginskii[11] on the oxidation $CO + O_2$ on MnO_2. The Elovich law applies to that phase of the reaction where the oxidation takes place predominantly at the expense of the active-O content of the catalyst which acts as a solid oxidant and loses its excess oxygen in the process. If only one O atom were consumed for each CO_2 molecule formed, one should expect simple first-order kinetics which is not found. It must be that active oxygen centers disappear from the surface over and beyond their direct consumption: this is the essence of our interpretation of the Elovich law for catalytic reactions.

The rate of decay of the active center density being proportional to α, it is obvious that with α very small, this decay may become unobservable, and at the limit $\alpha = 0$ it is absent. This is evidently the case in the course of the $H_2 + D_2$ exchange on Fe, studied by Farkas.[2]

6. Rate Law for the Opening Step.—If the rate of the reaction is determined by that of the opening step, it involves, besides the active center density produced by the first (center-making) reactant, also the mass action of the gaseous second reactant. This second reactant may, on the other hand, be an inhibitor as far as the active center density is concerned. On account of this dual role, this second reactant will introduce *two* factors into the rate expression. One, expressing its mass action as gaseous reactant, is simply its concentration to the first power. The question arises as to how to formulate its center-unmaking effect.

In the classic view, inhibition by a reactant consists simply in strong adsorption and correspond-

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[10] W. E. Garner, F. S. Stone and P. F. Tiley, *Proc. Roy. Soc.* (*London*), **A211**, 472 (1952).

[11] S. Z. Roginskii and R. S. Tselinskaya, *Zhur. fiz. Khim.*, **22**, 1350 (1948).

ingly strong monopolization of the surface by that reactant. There is no direct evidence for it, and there are grounds to doubt it. On Pease's[1] Cu catalyst, a poor adsorbent for hydrogen, the amounts of C_2H_4 adsorbed are only 3–5 times as great as the amounts of H_2; this is far from a "monopolization" of the surface and overwhelmingly strong adsorption of the inhibiting reactant. In the same system, C_2H_6, which is almost as much adsorbed as C_2H_4, does not inhibit at all. External catalyst poisons often inhibit strongly in amounts much too minute to correspond to any serious surface coverage. One is thus led to the conclusion that inhibition, be it by a reactant, a product, or an external poison, can go well beyond simple surface coverage, and consists in an initiation of active center self-annihilation. If so, one is tempted to express it by an Elovich-type formula, $n = n_0e^{-\alpha z}$, where now n_0 is the active center density in the absence of inhibitor, and z the amount of inhibitor adsorbed. There is direct evidence for it in the case of poisons in Roginskii's[12] determinations of the rate of the catalytic oxidation of isooctane on NiO as a function of the amount of poison (B_2O_3) adsorbed on the catalyst, and which can be exactly described by this exponential law. It means that the inhibitor does not inactivate by mere surface occupancy, but by causing widespread active center annihilation such as underlies our interpretation of the Elovich law. It appears plausible to extend this formulation also to nonextraneous inhibitors, including reactants and products.

Taking the $C_2H_4 + H_2$ reaction as an illustration of the first instance, designating by x the gas-phase concentration $[C_2H_4]$, and expressing the amount z of C_2H_4 adsorbed by a Freundlich function $z = x^m$ (where m is a true fraction), one can describe the effect of $[C_2H_4]$ by a function of the form $xe^{-\alpha x^m}$ where the first factor corresponds to the mass action of C_2H_4 as the gaseous reactant in the opening step, H(ads) + C_2H_4(gas), and the second factor expresses the inhibition through annihilation of H(ads) centers by C_2H_4. This function satisfies the observed facts, specifically the rise of initial rate with increasing initial x as long as x remains low, the passage of the rate through a maximum, and its fall with increasing excess of C_2H_4. Combining this function of $[C_2H_4]$ with the near first order in $[H_2]$ (due to its center-making effect), one gets for the initial rate of the opening step an expression of the form $k[H_2]^n \cdot [C_2H_4]e^{-\alpha[C_2H_4]^m}$ (with $n < 1$), which empirically and numerically can simulate some negative fractional order in $[C_2H_4]$. Laidler's[13] argument that the rate maximum at a certain concentration of C_2H_4 is proof of the Langmuir mechanism of this reaction, *i.e.*, of a reaction between adsorbed H and adsorbed C_2H_4, loses its validity.

In Jungers'[8] reaction $CO + H_2 \rightarrow CH_4, H_2O$, we consider the active centers to be H(ads), with CO reacting from the gas phase in the opening step H(ads) + CO(gas) → HCO(ads), but also depressing the initial active-center density through center annihilation. It will be noted that in this view, contrary to current interpretation, CO is a reactant only if captured on top of H(ads); if adsorbed directly on the surface, it becomes an inhibitor. The same considerations apply in this case as in the above instance of $C_2H_4 + H_2$. The apparently paradoxical fact that, while in the system $CO_2 + H_2$ the reaction on the same catalyst is faster than in $CO + H_2$, but that in the mixed system $CO + CO_2 + H_2$ the slower reaction, $CO + H_2$, proceeds first, at a rate equal to that in pure $CO + H_2$, is easily explained in our scheme which assumes H(ads) to be the *only* active centers at the surface: on account of the center-inhibiting effect of CO, the surface density of H(ads) centers is much higher in $CO_2 + H_2$ than in $CO + H_2$ or $CO + CO_2 + H_2$, and it is the same in the last two cases. On the other hand, of the two opening steps, H(ads) + CO(gas) and H(ads) + CO_2(gas), it is plausible to assume that the former is faster; the over-all rate in $CO_2 + H_2$ is faster despite the relative slowness of the opening step, thanks to the higher density of H(ads). In the mixed system, the faster opening step will obviously proceed first.

As an example of an inhibition by a product, one can point to the decomposition of NH_3 on doubly promoted Fe, most extensively studied by Love and Emmett.[14] The empirical rate law, $[NH_3]^{0.6}/[H_2]^{0.9}$, has been demonstrated to apply over small extents of conversion, in systems with varying proportions of NH_3 and of H_2 admixed in advance which simulates a more advanced stage of the conversion only as far as the gas composition but not as far as the catalyst is concerned. The experimental data verify this law with respect to near-initial conversions; there is nothing to bear out the applicability of the same law to the course of the reaction, which remains open. One is entitled to view the positive order in NH_3 as due to the center-making role of this reactant, and the -0.9 order in H_2 as a numerical approximation of a function $e^{-\alpha[H_2]^m}$ ($m < 1$), expressing center annihilation by H_2. A decision on that point can be reached only if and when more ample experimental material becomes available, especially with respect to the law of the rate over a set of increasing degrees of conversion in the same system.

PRINCETON, N. J.

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(12) S. Z. Roginskii and N. J. Element, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 350 (1951).

(13) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 165.

(14) K. S. Love and P. H. Emmett, THIS JOURNAL, **63**, 3297 (1941).