

TABLE III
RELATIVE INERT GAS EFFICIENCIES FOR SOME UNIMOLECULAR REACTIONS

Inert gas	Reacting molecule						
	CH ₃ NC	Cyclopropane ^c	Cyclobutane ^c	N ₂ O ₃ ^c	N ₂ O ^c	NO ₂ Cl ^e	cis-butene-2 ^f
Ar	[0.05 ^a]	0.07	0.21	0.15	0.20	0.21	0.08
N ₂	.25 ^b	0.07	0.21	0.23	0.24	0.29	0.32
C ₂ H ₆	.6 ^b
Methane	...	0.24	0.38
Propylene	...	~1.0 ^d

^a Assumed in this paper. ^b Ref. 1. ^c A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths Scientific Publications, London, 1955, p. 84. ^d H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc. (London)*, **A217**, 563 (1953). ^e Ref. 6 in this paper. ^f R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **57**, 2226 (1961).

in the fall-off region for the excitation of molecular vibrations, in the high temperature regime.

Acknowledgments.—This work was supported by the AFOSR, Grant No. AF-AFOSR-103-63, to whom grateful acknowledgment is made. The authors are in-

debted to Professor B. S. Rabinovitch for supplying details of the methyl isocyanide synthesis, and to Dr. Chava Lifshitz for help with the Fortran programs. H. F. C. wishes to thank the National Science Foundation for a Cooperative Fellowship during part of this work.

[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL CO., MIDLAND, MICH.]

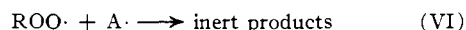
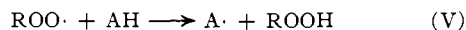
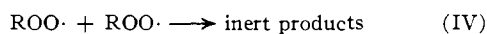
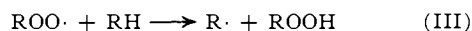
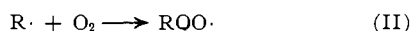
Antioxidant Inhibition by Phenol^{1a}

BY W. G. LLOYD^{1b} AND C. E. LANGE

RECEIVED AUGUST 26, 1963

The kinetics of oxidation retardation by the weak antioxidant phenol has been examined for two systems. Under nonbranching conditions retarded rates are proportional to the square root of initiator concentration and to the inverse square root of phenol concentration, as previously found by Hammond, Boozer, *et al.* The dependence of retarded rate upon substrate concentration in both nonbranching and branching systems is inconsistent with the complex termination mechanism. A hypothesis of "selective inhibition" is proposed.

Inhibition by phenolic antioxidants has been accounted for in terms of a straightforward transfer of the phenolic hydrogen atom to the chain carrier peroxy radical, thus forming a resonance-stabilized aryloxy radical which is incapable of continuing the kinetic chain.^{2,3} Thus from the reaction scheme



where IN, RH, and AH denote initiator, substrate, and antioxidant, respectively, the retarded rate (assuming that reaction IV may be ignored)⁴ is

$$-d(\text{O}_2)/dt = 2nk_1(\text{IN}) + (nk_1k_3(\text{IN})(\text{RH})/2k_5(\text{AH})) \quad (1)$$

This interpretation has been fruitful, *e.g.*, in deriving initiation rates from the observed retardation of weakly inhibited systems.⁵ Several recent kinetic studies of autoxidation inhibition⁶ and of polymerization inhi-

bition with^{7,8} and without⁹ oxygen present have been interpreted in terms of this simple radical transfer termination process. This view is further supported by evidence that antioxidant efficacy of substituted phenols may be correlated with Hammett σ -values,¹⁰ phenolic O-H stretching frequencies,¹¹ the calculated stabilities of phenol-alkylperoxy radical "frontal" charge-transfer complexes,¹² ease of phenolic H-abstraction by diphenylpicrylhydrazyl radicals,¹³ oxidation potentials,^{2,3,14,15} and electrophilic substituent values.¹⁵

Clear indication of a greater kinetic complexity was afforded in the demonstration by Hammond, Boozer, and co-workers¹⁰ that for such systems as tetralin in chlorobenzene at 62.5° with 2,2'-azobis(isobutyronitrile) (ABIN) and with a weak antioxidant such as phenol, retarded rates were proportional to the square root of initiator concentration and to the inverse square root of retarder concentration. These "anomalous" dependencies led to the proposal of a two-step termination mechanism, consisting of the fast, reversible formation of a complex between antioxidant molecule and peroxy radical followed by a slower, irreversible

(1) (a) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. (b) Present address: The Lumms Co., Newark 14, N. J.

(2) J. L. Bolland and P. ten Have, *Trans. Faraday Soc.*, **43**, 201 (1947).

(3) J. L. Bolland and P. ten Have, *Discussions Faraday Soc.*, **2**, 252 (1947).

(4) This commonly made assumption is reasonable if (and only if) the retarded rate is less than about one-quarter of the unretarded oxidation rate.

(5) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, **A198**, 252 (1949).

(6) C. E. H. Bawn and J. E. Jolley, *ibid.*, **237**, 297 (1956); G. W. Kennerly and W. L. Patterson, Jr., *Ind. Eng. Chem.*, **48**, 1917 (1956); A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956); 2217 (1957); J. R. Shelton and E. T. McDonel, *J. Polymer Sci.*, **32**, 75 (1958).

(7) B. A. Dolgoplosk and G. A. Parfenova, *Zh. Obshch. Khim.*, **27**, 3083 (1957); R. G. Caldwell and J. L. Ihrig, *J. Polymer Sci.*, **46**, 506 (1960); A. B. Raevskii, V. G. Kryuchkova, and S. V. Zavgorodnii, *Vysokomol. Soed.*, **3**, 1121 (1961).

(8) R. G. Caldwell and J. L. Ihrig, *J. Am. Chem. Soc.*, **84**, 2878 (1962).

(9) M. P. Gotsay, G. A. Harpell, and K. E. Russell, *J. Polymer Sci.*, **67**, 641 (1962).

(10) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3238 (1955).

(11) D. S. Davies, H. L. Goldsmith, A. K. Gupta, and G. R. Lester, *J. Chem. Soc.*, 4926 (1956).

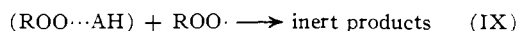
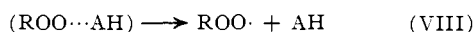
(12) T. Fueno, T. Ree, and H. Eyring, *J. Phys. Chem.*, **63**, 1940 (1959).

(13) J. C. McGowan and T. Powell, *J. Appl. Chem.*, **12**, 1 (1962).

(14) J. F. Hedenberg, Preprints, American Chemical Society, Division of Petroleum Chemistry, Vol. 7, No. 3, 1962, p. 75.

(15) W. G. Lloyd and R. G. Zimmerman, unpublished observations.

reaction of this complex with a second peroxy radical to yield inert products^{10,16}



For the scheme represented by reactions I–III and VII–IX, the steady-state retarded rate is

$$-d(\text{O}_2)/dt = 2nk_1(\text{IN}) + (nk_1k_8/2k_7k_9)^{1/2} \times k_3(\text{IN})^{1/2}(\text{RH})(\text{AH})^{-1/2} \quad (2)$$

For other than very strong retardation, the first term on the right-hand side may be ignored, and eq. 2 then conforms to the observed¹⁰ relationships

$$-d(\text{O}_2)/dt = K(\text{IN})^{1/2}(\text{AH})^{-1/2} \quad (3)$$

Support for this complex termination mechanism has come from a number of recent studies.¹⁷

There are at least two respects in which our current understanding of inhibition by simple phenols appears to be incomplete: (a) There exist two different kinds of actual behavior in nonbranching retarded systems, characterized by integral-order and half-order dependencies, and two quite different mechanisms (noted above), neither of which is a special case of the other. The state of the theory consequently lacks predictive power; we cannot be sure, for any new substrate-retarder system, which mechanism to invoke until we have obtained empirical knowledge of the kinetics of that particular system. (b) Notwithstanding the persuasive support for the existence of half-order dependencies,^{10,16,17} the explanation of these dependencies encounters grave problems when applied to polymeric substrates: the conjunction of two polymeric peroxy radicals is a very improbable occurrence to be used to explain effective retardation, and yet it is equally unattractive to adopt a purely discretionary restriction upon the scope of a mechanism simply to avoid this paradox. The present work attempts to contribute to the resolution of this general problem.

Experimental Results

To re-examine the kinetic dependencies of phenol-retarded autoxidations, the system tetralin–diphenyl oxide–ABIN–phenol was examined at 70.7°. Initial autoxidation rates are shown in Table I. The dependency of retarded rate upon initiator and phenol concentrations is seen to conform closely to eq. 3, thus confirming the half-order dependencies previously found¹⁰ for similar systems. The substrate power dependency of 1.48 ± 0.08 fails, however, to conform to the predictions of the complex termination mechanism (eq. 2).

To establish the general character of these dependencies with phenol, a second system was also examined, with cyclohexene replacing tetralin as substrate and *t*-butylbenzene replacing diphenyl oxide as diluent. Retarded rates at 60.6° were subject to initial irregularities which impaired the precision (but in no case significantly altered over-all dependencies). The more consistent 1-hr. retarded rates are shown in Table II. These dependencies are identical, within experimental error, with those of Table I.

These data are obtained under nonbranching conditions. Tetralyl hydroperoxide is stable at 70°¹⁸ and cyclohexene-3-

(16) C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954); C. E. Boozer, G. S. Hammond, C. E. Hamilton, and C. Peterson, *ibid.*, **77**, 3380 (1955).

(17) O. L. Harle and J. R. Thomas, *ibid.*, **79**, 2973 (1957); K. U. Ingold, *J. Inst. Petroleum*, **45**, 244 (1959); G. S. Hammond and U. S. Nandi, *J. Am. Chem. Soc.*, **83**, 1217 (1961); J. R. Thomas and C. A. Tolman, *ibid.*, **84**, 2930 (1962).

(18) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574, 1578 (1948).

TABLE I

PHENOL-RETARDED AUTOXIDATION OF TETRALIN^a

ABIN concn., M × 10 ²	Phenol concn., M × 10 ²	Tetralin concn., M	Initial rate, mm./min.	Power dependency ^b
0.609	4.00	6.58	0.175	
1.218	4.00	6.58	.265	+0.52
2.436	4.00	6.58	.400	
3.654	4.00	6.58	.455	(±0.032)
4.872	4.00	6.58	.510	
6.090	0.80	2.63	.485	
6.090	1.60	2.63	.340	-0.52
6.090	3.20	2.63	.237	
6.090	6.40	2.63	.173	(±0.013)
6.090	12.00	2.63	.117	
6.090	4.00	1.97	.117	
6.090	4.00	2.63	.189	
6.090	4.00	3.29	.238	+1.48
6.090	4.00	3.95	.301	
6.090	4.00	4.61	.382	(±0.080)
6.090	4.00	5.26	.550	
6.090	4.00	5.26	.505	

^a At 70.7° (std. dev. ±0.067°) with diphenyl oxide as diluent.

^b Least-squares value of n for $-d(\text{O}_2)/dt = k(V)^n$ where V is the concentration variable; standard deviation of n shown in parentheses.

hydroperoxide at low concentrations is stable at 60°. The stability of the latter and the inability of phenol to induce heterolytic decomposition under these conditions was confirmed by maintaining solutions of oxidized cyclohexene (containing 0.42 *N* cyclohexenyl hydroperoxide) at 60.5° without phenol and with 1 × 10⁻³ *M* and 1 × 10⁻² *M* phenol added. After 66 hr. the hydroperoxide concentrations were not perceptibly changed in any of the samples.

The substitution of a branching catalyst for ABIN may be expected to modify significantly the inhibition kinetics.²⁰ When cobaltous naphthenate replaces ABIN in the present systems, the rate dependency upon phenol concentration shifts cleanly from inverse square root to inverse first order (Table III). At constant concentrations of cobalt soap and of phenol these data also show a very steep dependency of rate upon cyclohexene concentration; the indicated power dependency is +2.6 (±0.2).

Discussion

The data of Tables I and II show a three-halves power dependency of retarded rate upon substrate concentration. Mahoney and Ferris²¹ in substantially concurrent¹ work find precisely the same dependency for chlorobenzene solutions of tetralin at 60° with several concentrations of phenol. This, it has been observed,^{1,21} is inconsistent with the requirements of the complex termination mechanism. Under branching conditions the substrate power dependency of about 2.6 is considerably higher than can be accounted for by that mechanism. These discrepancies, taken together with recently strengthened evidence²² for kinetic isotope effects in phenolic antioxidant inhibition, cast serious doubt upon the validity of the complex termination mechanism as a satisfactory explanation for the half-order dependencies observed in certain weakly retarded systems.

Mahoney and Ferris²¹ have proposed a special case of transfer-re-entry²³ to account for the three-halves

(19) L. Bateman, H. Hughes, and A. L. Morris, *Discussions Faraday Soc.*, **14**, 190 (1953).

(20) W. T. Lippincott and W. G. Lloyd, *J. Am. Chem. Soc.*, **79**, 4811 (1957); H. S. Blanchard, *ibid.*, **82**, 2014 (1960); P. L. Weinle, "Autoxidation Inhibition in Cumene," Thesis, University of Florida, 1961; N. Michaels, "Autoxidation Inhibition in Tetralin," Thesis, University of Florida, 1961.

(21) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2345 (1963).

(22) K. U. Ingold and J. A. Howard, *Nature*, **195**, 280 (1962); J. R. Shelton and D. N. Vincent, Preprints, American Chemical Society, Division of Polymer Chemistry, Vol. 4, No. 1, 1963, p. 292.

TABLE II

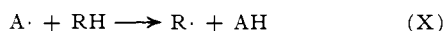
PHENOL-RETARDED AUTOXIDATION OF CYCLOHEXENE^a

ABIN concn., $M \times 10^2$	Phenol concn., $M \times 10^2$	Cyclohexene concn., M	1-hr. rate, mm./min.	Power dependency ^b
1.52	0.600	3.945	0.207	+0.58
4.57	.600	3.945	.360	
6.09	.600	3.945	.402	(±0.07)
12.18	.600	3.945	.720	
6.09	.100	3.945	.966	-0.50
6.09	.300	3.945	.570	
6.09	.600	3.945	.402	(±0.009)
6.09	1.000	3.945	.303	
6.09	0.600	2.959	.273	
6.09	.600	3.945	.402	+1.42
6.09	.600	4.932	.582	
6.09	.600	5.918	.718	(±0.03)
6.09	.600	7.891	1.100	

^a At 60.55° (std. dev. ±0.15°) with *t*-butylbenzene as diluent.

^b See Table I, note *b*.

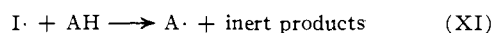
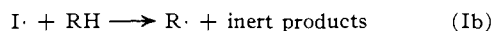
dependency, postulating a competition between reactions VI and X for the inhibitor-derived radical



This scheme leads to a rate equation predicting the observed dependencies for nonbranching systems, provided that the kinetic chain length is long and that radical destruction proceeds exclusively by cross-termination (reaction VI). Since their mechanism presents certain problems in interpretation,²⁴ and since we have been unable to account for branching system kinetics in terms of this postulate, we have sought an alternate hypothesis to account for the observed kinetics.

The ease of H-abstraction from phenols by free radicals has been found to vary dramatically with phenol structure and reactivity.^{13,25} It is suggested, therefore, that while reactive phenols may transfer readily with any oxidizing radical, phenol itself may be much more selective; as a limiting case, phenol may react with the "hot" precursor radicals but be incapable of reacting effectively with the carrier radicals of certain oxidizing systems. An instance of the selective reaction of the more reactive of two coexistent species of hydrocarbon radicals has been recently reported by Kochi and Rust.²⁶ A kinetically similar proposal has been advanced by Funt and Williams to explain certain polymerization retardation phenomena.²⁷

This hypothesis requires that reaction I be considered in its elementary steps and that termination proceed substantially by reactions IV and XI.



Here $I \cdot$ is the hydrogen-abstracting radical derived

(23) Cf. A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953); 2215 (1956); 2217 (1957).

(24) For example, the re-entry postulate requires, in order to generate the observed dependencies, that the propagation chain length be long and that reaction IV be negligible. Yet the observed dependencies²¹ are found at retarded rates in excess of one-half of the unretarded rate, thus demonstrating steady-state concentrations of (ROO·) such as to require the inclusion of reaction IV.

(25) J. C. McGowan, T. Powell, and R. Raw, *J. Chem. Soc.*, 3103 (1959); J. C. McGowan and T. Powell, *ibid.*, 2160 (1961); J. S. Hogg, D. S. Lohmann, and K. E. Russell, *Can. J. Chem.*, 39, 1588 (1961).

(26) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, 84, 3946 (1962).

(27) B. L. Funt and F. D. Williams, *J. Polymer Sci.*, 67, 711 (1962).

TABLE III

PHENOL-RETARDED AUTOXIDATIONS UNDER BRANCHING CONDITIONS

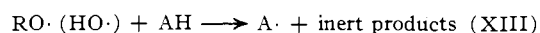
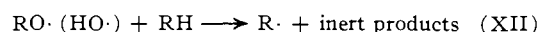
Cobalt concn., $M \times 10^5$	Phenol concn., $M \times 10^2$	Substrate	Substrate concn., M	Oxidation rate, mm./min.	Power dependency ^b
2.50	0.60	Tetralin ^c	6.51	0.565	
2.50	1.00	Tetralin ^c	6.51	.400	-0.95
2.50	1.40	Tetralin ^c	6.51	.280	
2.50	2.00	Tetralin ^c	6.51	.177	(±0.067)
2.50	2.60	Tetralin ^c	6.51	.150	
2.50	0.200	Cyclohexene ^d	9.765	.847	
2.50	.400	Cyclohexene ^d	9.765	.515	-1.00
2.50	.600	Cyclohexene ^d	9.765	.317	
2.50	1.000	Cyclohexene ^d	9.765	.179	(±0.05)
2.50	2.000	Cyclohexene ^d	9.765	.090	
10.00	0.600	Cyclohexene ^d	2.959	.040	
10.00	.600	Cyclohexene ^d	3.945	.120	+2.58
10.00	.600	Cyclohexene ^d	5.918	.345	
10.00	.600	Cyclohexene ^d	7.891	.583	(±0.20)
10.00	.600	Cyclohexene ^d	9.469	.862	

^a Cobaltous naphthenate, added as a $2.50 \times 10^{-3} M$ concentrate in diphenyl oxide. ^b See Table I, note *b*. ^c See Table I, note *a*. ^d See Table II, note *a*.

from the initiator; in this case, recent evidence that acetone cyanohydrin is the major product of ABIN decomposition in oxygenated systems²⁸ suggests that $I \cdot$ may be the 2-cyano-2-propoxy radical. For this limiting case the steady-state rate for other than strongly inhibited systems is

$$-d(O_2)/dt = k_3(nk_{1a}k_{1b}/2k_4k_{11})^{1/2}(IN)^{1/2}(RH)^{1/2}(AH)^{-1/2} \quad (4)$$

subject only to the requirement (necessary to afford significant retardation) that reaction XI proceeds more rapidly than reaction Ib.²⁹ For the case of catalyzed homolysis of the hydroperoxide to product $RO \cdot$ (and perhaps $HO \cdot$) radicals, the competition between reactions Ib and XI is replaced by the competition between reactions XII and XIII



where again, to obtain significant inhibition, reaction XIII must dominate reaction XII. This leads, in the limiting case of no reaction between phenol and alkylperoxy radicals, to

$$-d(O_2)/dt = k_3^2k_{12}(RH)^3/k_4k_{13}(AH) \quad (5)$$

which is the only derivation we have found to yield substrate dependencies as high as that encountered in Table III. If this hypothesis is correct, the observed less than cubic dependency may be due to a side reaction, e.g., a feeble transfer between phenol and carrier peroxy radical.

Experimental

Tetralin and diphenyl oxide (best commercial grades) were fractionated under purified nitrogen and center cuts collected;

(28) J. C. Bevington and H. G. Troth, *Makromol. Chem.*, 53, 200 (1962).

(29) This hypothesis essentially proposes that the relative reactivities of substrate and phenol be quite different toward the initiator-derived $I \cdot$ radical than toward the chain-carrier $ROO \cdot$ radical. Where different kinds of attacking radicals are involved, such differences are common.³⁰ If $I \cdot$ were a peroxy radical, however, such difference in relative reactivities would be unusual.

(30) Recent examples of significant differences are reported by C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, 85, 3129 (1963), and by G. A. Russell and C. DeBoer, *ibid.*, 85, 3136 (1963).

t-butylbenzene and cyclohexene were reagent grade samples obtained from Phillips Petroleum Co. All were found to be well over 99.5% pure by gas chromatography. Redistilled phenol (Dow Chemical Co.) was a colorless crystalline solid with no impurities detectable by gas chromatography. Cobalt naphthenate was Nuodex Product Co. Nuodex Co 6. 2,2'-Azobis(isobutyronitrile) (ABIN) was obtained from E. I. du Pont de Nemours Co., stored under refrigeration, and used without further purification. Standard solutions were prepared containing phenol in substrate, ABIN in inert diluent, and cobalt soap in

inert diluent; these were stored in a light-shielded, purged, argon-padded system from which portions were withdrawn and combined volumetrically for each run. Oxidations were carried out in a constant-volume semistatic apparatus described previously.³¹

Acknowledgment.—We wish to thank one of the referees for valuable criticism of the original manuscript.

(31) W. G. Lloyd, *J. Am. Chem. Soc.*, **78**, 72 (1956); *J. Chem. Eng. Data*, **6**, 541 (1961).

[CONTRIBUTION FROM THE PROCESS RESEARCH DIVISION, ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Chemisorption and Surface Chemistry of Ethylene on Supported Platinum Catalysts

By P. J. LUCCHESI, J. L. CARTER, AND J. H. SINFELT

RECEIVED OCTOBER 19, 1963

The chemisorption and surface chemistry of ethylene on Pt-Al₂O₃ catalysts have been studied and compared with previously reported results on ethylene over Al₂O₃. The same types of species are formed on the Pt-Al₂O₃ catalysts as are formed on the Al₂O₃ alone, but the reactivities of the adsorbed species are greatly different. On treatment with H₂, the adsorbed species were removed much more readily from the Pt-Al₂O₃ catalysts than from the Al₂O₃ alone. The desorption products resulting from the H₂ treatment consist largely of ethane and *n*-butane at the lower temperatures investigated (100–150°), but increasing amounts of methane and propane are formed at the higher temperatures, where rupture of C–C bonds becomes important. The much greater ease of removal of the adsorbed species from Pt-Al₂O₃ catalysts on H₂ treatment suggests that migration of reactive species between Pt and Al₂O₃ centers may be important.

Supported platinum catalysts are of great technical interest for a variety of hydrocarbon reactions. When the platinum is supported on an acidic oxide such as alumina or silica-alumina, the catalyst is termed bifunctional, *i.e.*, the catalyst has the properties of both a hydrogenation-dehydrogenation catalyst and an acidic catalyst. It has been amply demonstrated that certain reactions over these bifunctional catalysts, including the isomerization of alkanes¹ and the dehydroisomerization of methylcyclopentane,^{2,3} involve the cooperative action of the platinum centers and the acidic centers of the catalyst. Furthermore, recent studies suggest that the hydrogenation of ethylene over mixtures of Pt-SiO₂ and Al₂O₃ catalysts may involve a cooperative action of separate centers on the two catalysts.⁴

In view of the well established bifunctional nature of Pt-Al₂O₃ in the catalysis of certain hydrocarbon reactions, the question arose whether the presence of a small amount of platinum could significantly affect the nature of chemisorption of a molecule such as ethylene on Al₂O₃, or alter the subsequent reactivity of the chemisorbed species on the Al₂O₃. Consequently, in the present work it was decided to investigate the chemisorption and surface chemistry of ethylene on Al₂O₃ containing small amounts of platinum. The chemisorption of ethylene on alumina itself has previously been studied with the use of infrared spectroscopy, and the reactivity of the chemisorbed species with hydrogen determined.⁵ The results of the present paper represent an extension of this work. The main emphasis in the present study, however, has been on the reactivity of the chemisorbed species rather than

with infrared measurements of the nature of the chemisorption process.

Experimental

Apparatus and Procedure.—The experiments were carried out in a cell specially designed for use with a Beckman IR-7 double-beam grating spectrometer. A detailed description of the apparatus, along with the sample preparation procedure, has been reported previously.⁵ Although the details of the infrared spectra were of secondary interest in the present work, it was convenient to do the experiments in this apparatus. Furthermore, the spectra were of use in giving information about the extent of removal of adsorbed species after treatment with hydrogen.

The Pt-Al₂O₃ catalysts used in the present work were pretreated as follows, prior to adsorption of the ethylene: The catalysts were slowly heated to 500° while they were being evacuated. When the pressure was 5×10^{-6} mm., hydrogen was admitted to the sample cell. The sample was then reduced for 0.5 hr. at 500°, and was subsequently evacuated to 5×10^{-6} mm. at 500°. This pretreating procedure is similar to that described by Spenadel and Boudart.⁶

After the cell was cooled to room temperature under vacuum, the background spectrum of the sample was recorded. The ethylene was then admitted to the sample cell and the spectrum again recorded. The spectra were also recorded after various intervals of time up to several days. At certain times the unadsorbed ethylene was removed from the sample cell by evacuation at room temperature and the spectrum of the adsorbed species recorded.

After the adsorption part of the experiment was completed, the hydrogenation of the adsorbed species was investigated. This was done by heating the sample to the desired hydrogenation temperature and then admitting hydrogen to the cell at a pressure of 18 cm. The hydrogenation temperatures varied from 150 to 450° and the reaction times from 20 min. to 2 days. At the end of the hydrogenation period, the gaseous material containing the desorbed products was drawn into a liquid nitrogen trap. The contents of the trap were then analyzed with a capillary gas chromatographic column employing a flame ionization detector. This technique can detect hydrocarbons in the parts per million range, and was necessary because of the very small amount of product available for the analysis. After the desorbed products were removed from the cell, the sample was cooled to room temperature and the infrared spectrum recorded.

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