

ing the required yield of H₂. A similar decomposition has been observed for C₂H₅Br.¹⁵

I⁺.—The following sets of neutral fragments from C₂H₅I are energetically allowed: C₂H₃ + H₂, CH₄ + CH, CH₃ + CH₂ (all approximately thermo-neutral), C₂H₅ ($\Delta H = -58$ kcal.) and C₂H₄ + H ($\Delta H = -17$ kcal.). The first three would produce excessive amounts of measurable products. Either of the last two possibilities is acceptable. The latter was chosen.

CI⁺.—In this case, and in those which follow, the primary ion appears in the spectra of both CH₃I and of C₂H₅I. Simultaneous solution of the two thermochemical equations establishes which processes are allowed. If CH₃I⁺ → CI⁺ + H₂ + H, then from C₂H₅I either CH₃ + 2H or CH + 2H₂ or CH₂ + H₂ + H may result. The choice is not critical and the last is chosen.

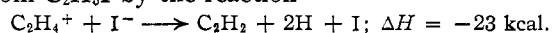
CH₂I⁺.—The appearance potentials of I⁺ and of CH₂I⁺ from CH₃I are indistinguishable and either may be the parent ion of I₂⁺ observed in the secondary spectrum. Since I⁺ does not react with C₂H₅I to yield I₂⁺ and C₂H₅, we shall assume that I⁺ and CH₃I do not form I₂⁺ and CH₃. A more compelling reason for choosing CH₂I⁺ + CH₃I → I₂⁺ + C₂H₅ is that it accounts for C₂H₅ formation. The neutral fragment accompanying primary CH₂I⁺ from C₂H₅I is somewhat uncertain because simultaneous solution of the thermochemical equations gives no thermo-neutral process. If CH₃ is produced, 38 kcal. of kinetic energy must be dissipated but smaller fragments are not allowed from the measured appearance potentials.

Insofar as ionic processes produce molecular species uniquely, the observed yields are well defined. The yield of H₂ from iodine-containing solutions may be the only example. In both systems HI forms molecularly and also by reaction between H + RI and, for ethyl iodide, C₂H₅ + I. Calculated yields of H and of HI are therefore combined in Table V. Since HI is also lost by HI + R → HR + I, the "observed"

yields of HI in Table V are based upon the sum HI + RH.

For ethyl iodide an additional, but unknown, correction should be allowed for C₂H₅ + I → HI + C₂H₄. These reactions occur to a considerable extent within spurs, for which the yields are not accurately measurable. We shall assume that $\Delta G(C_2H_4)$ and $\Delta G(HI)$ resulting from the addition of large concentrations of iodine or hydrogen iodide (Tables II and III) represented 50% of the spur reaction. The average change observed for ethylene, combining data of Tables II and III, was 5.5×10^{-6} mole. Analysis for hydrogen iodide was inaccurate but the assumed mechanism requires the same change for hydrogen iodide and for ethylene. Reaction within the spurs therefore produces roughly 10^{-5} mole of each. Observed results have been adjusted accordingly.

There is no evident source of C₂H₂ in either system, but one may speculate that it originates from C₂H₅I by the reaction



Calculated and observed abundances would be 1.2 and 1.3, respectively. All observed yields in Table V have been referred to CH₃ or C₂H₅ measured as CH₄ or C₂H₆ at high concentrations of HI.

It is difficult to assess the significance of the comparisons in Table V because of the necessity of choosing among multiple possibilities in several instances. Decompositions involving as many as three or four fragments, and presumably occurring consecutively, must be made in about four instances. For the liquid phase this may appear quite implausible. It is a fact, however, that liquid methyl iodide produces small but significant yields of H₂, C₂H₂ and C₂H₄, while liquid ethyl iodide similarly yields H₂, C₂H₂ and CH₂I₂ which imply complex decompositions. The evidence for ion-molecule reactions in the liquid phase is not strong, since the almost invariable product is the major free radical species and agreement within a factor of two must be regarded as excellent.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Conformational Analysis of Radical Abstraction of Hydrogen Atoms from Aromatic Hydrocarbons¹

By J. A. MEYER, V. STANNETT AND M. SZWARC

RECEIVED MAY 27, 1960

The relative rate constants of H abstraction by methyl radicals were determined for a series of aromatic hydrocarbons. Comparison of the respective rate constants involving other radicals, such as ROO·, *t*-BuO·, CCl₂· and polystyryl, with methyl radicals reveals an extraordinarily good numerical agreement between the corresponding relative rate constants. Consideration of the interaction between the non-bonded H atoms shows that the reactivities of ethyl benzene and cumene are lower than anticipated because of the strain in the respective transition states. On the other hand, axial α C-H's in tetralin correspond to "normal" reactivities. It was shown that the ratio of reactivities of aliphatic primary:secondary:tertiary C-H's corresponds to that in the aromatic series if "normal" C-H are considered. This correlation applies also to olefinic series if the effects of strain are taken into account.

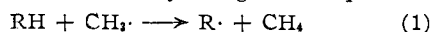
The studies of Russell on the oxidation of hydrocarbons^{2a} and of Williams, Oberright and Brooks²

on the reactions of *t*-butoxy radicals drew our attention to an interesting observation, namely that the abstraction of hydrogen atoms by ROO· or *t*-BuO· radicals seems to proceed faster with indan or tetralin than with ethylbenzene. The reactive hydro-

(1) This work was supported by the A.C.S. Petroleum Fund.

(2) (a) G. A. Russell, *THIS JOURNAL*, **78**, 1047 (1956). (b) A. L. Williams, E. A. Oberright and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

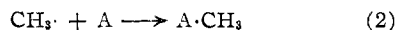
gens in all these compounds belong to the same class of secondary hydrogens α to the benzene ring, and hence the appreciable difference in their reactivities calls for further study. The problem is what causes tetralin or indan to be more reactive than ethylbenzene; are these results due to specific selectivity of RO_2 or $t\text{-C}_4\text{H}_9\text{O}$ radicals or are they a genuine reflection of the higher reactivity of C-H bonds that are attached to a ring structure? With a hope of shedding more light on this problem, we undertook studies of reactions described by the general equation



for a series of aromatic hydrocarbons that include ethylbenzene, indan and tetralin. Our results, summarized in Table II, confirm the previous observations and demonstrate again the high reactivity of the C-H bonds in tetralin and indan.

Experimental

The hydrogen abstraction reactions were studied in the liquid phase at 65° , and in each experiment the hydrocarbon to be investigated was used as the solvent. The thermal decomposition of acetyl peroxide served as a source of methyl radicals, the concentration of the peroxide being about $10^{-2} M$. The relative rate constants of the abstraction reaction were determined by a competitive technique, reaction 2



competing with reaction (1) for methyl radicals. *trans*-Stilbene and 1,1-diphenyl ethylene were used as the "adding" agents A.

All the reagents were carefully purified and distilled before being used. The reactions were carried out in sealed glass ampules after prior degassing of their contents in a high vacuum. The details of experimental technique were described previously,^{3,4} and hence only a brief outline of the principles will be given here.

Samples of stilbene or 1,1-diphenylethylene dissolved in the pertinent hydrocarbon, each containing the same amount of the peroxide, were heated at 65° for exactly 2 hr. In every series of experiments the concentration of stilbene or 1,1-diphenylethylene was varied and, in addition, two samples, not containing these compounds, were used as "blanks." The amounts of methane and carbon dioxide formed in the decomposition were then determined, and from these data the respective k_1/k_2 were calculated by means of the equation

$$k_1/k_2 = (X_A/X_{HR}) \{ \text{CH}_{4f} \} / \{ \text{CH}_{4b} - \text{CH}_{4f} \}$$

where X_A and X_{HR} denote the mole fractions of A and HR, respectively, while CH_{4f} and CH_{4b} denote the amounts of methane formed in the presence and the absence of stilbene or 1,1-diphenylethylene. Alternatively, the ratio CH_4/CO_2 could be used instead of CH_4 . This method was verified previously and its justification is described in previous publications from this Laboratory.^{3,4,5}

Results and Discussion

The experimental data are given in Tables I and II. From these the relative rate constants of abstraction per active hydrogen are computed, toluene being taken as a standard. The relevant results are listed in Table III; the quoted averages are weighed according to the error of each determination.

Although the experimental uncertainties are larger than one would like them to be, the data presented in Table III permit one to draw a number of interesting conclusions. First of all, it is clearly demonstrated that the reactivity of primary C-H's

(3) M. Levy and M. Szwarc, *THIS JOURNAL*, **77**, 1949 (1955).

(4) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957).

(5) R. P. Buckley, F. Leavitt and M. Szwarc, *THIS JOURNAL*, **78**, 5557 (1956).

TABLE I
INVESTIGATED HYDROCARBON + *trans*-STILBENE; $T = 65^\circ$

Hydrocarbon	No. expt.	Range mole ratio of <i>trans</i> -stilbene/HR	$k_1/k_2 \times 10^3$ based on	
			CH_4/CO_2	CH_4
Toluene	5	0.65-2.0	2.59 ± 0.3	2.45 ± 0.3
<i>o</i> -Xylene	5	0.73-4.5	5.01 ± 0.14	4.78 ± 0.18
<i>m</i> -Xylene	5	1.0-4.0	5.50 ± 0.5	5.92 ± 0.7
<i>p</i> -Xylene	6	1.0-4.2	6.55 ± 1.0	5.54 ± 0.8
Mesitylene	5	2.3-7.9	8.75 ± 1.3	7.40 ± 0.3
Ethyl benzene	6	2.0-7.7	7.58 ± 0.95	7.59 ± 0.57
Cumene	5	4.0-13.1	12.5 ± 1.2	10.2 ± 0.8
Indan	6	2.7-14.6	34.8 ± 7	24.3 ± 10
Tetralin	—	—	—	—

TABLE II
INVESTIGATED HYDROCARBON + 1,1-DIPHENYLETHYLENE;
 $T = 65^\circ$

Hydrocarbon	No. expt.	Range mole ratio 1,1-diphenyl ethylene/HR	$k_1/k_2 \times 10^3$ based on	
			CH_4/CO_2	CH_4
Toluene	6	0.05-0.25	1.48 ± 0.05	1.50 ± 0.05
<i>o</i> -Xylene	5	.10-.40	$2.94 \pm .03$	3.06 ± 0.04
<i>m</i> -Xylene	6	.05-.20	$2.50 \pm .4$	2.74 ± 0.2
<i>p</i> -Xylene	5	.05-.20	$3.39 \pm .15$	3.68 ± 0.2
Mesitylene	6	.05-.43	$4.12 \pm .35$	3.71 ± 0.24
Ethylbenzene	5	.10-.40	$3.96 \pm .10$	4.11 ± 0.08
Cumene	9	.10-.90	$6.19 \pm .16$	6.34 ± 0.04
Indan	8	.10-1.8	18.2 ± 4	15.0 ± 3
Tetralin	7	.25-1.62	19.7 ± 3	26.5 ± 12

TABLE III
RELATIVE RATE CONSTANTS OF H ABSTRACTION PER ACTIVE H (TOLUENE STANDARD = 1)

Hydrocarbon	Competing with	$k_1' \text{HR} / k_1' \text{toluene}$ based on	
		CH_4	CH_4/CO_2
Toluene	Stilbene	(1.00)	(1.00)
	1,1-Diphenylethylene	(1.00)	(1.00)
	Weighed average	(1.00)	
<i>o</i> -Xylene	Stilbene	0.98 ± 0.15	0.97 ± 0.14
	1,1-Diphenylethylene	1.02 ± 0.15	1.00 ± 0.13
	Weighed average	0.99	
<i>m</i> -Xylene	Stilbene	1.26 ± 0.22	1.06 ± 0.21
	1,1-Diphenylethylene	0.92 ± 0.09	0.85 ± 0.19
	Weighed average	1.00	
<i>p</i> -Xylene	Stilbene	1.13 ± 0.26	1.27 ± 0.26
	1,1-Diphenylethylene	1.23 ± 0.07	1.15 ± 0.07
	Weighed average	1.19	
Mesitylene	Stilbene	1.00 ± 0.15	1.13 ± 0.35
	1,1-Diphenylethylene	0.83 ± 0.09	0.93 ± 0.12
	Weighed average	0.94	
Ethyl benzene	Stilbene	4.65 ± 1.0	4.40 ± 0.9
	1,1-Diphenylethylene	4.11 ± 0.2	4.02 ± 0.2
	Weighed average	4.14	
Cumene	Stilbene	12.5 ± 2.5	14.5 ± 2.5
	1,1-Diphenylethylene	12.7 ± 0.6	12.5 ± 1.0
	Weighed average	12.9	
Indan	Stilbene	7.2 ± 2.0	10.1 ± 5.0
	1,1-Diphenylethylene	7.5 ± 1.5	9.2 ± 1.5
	Weighed average	8.3	
Tetralin ^b	Stilbene
	1,1-Diphenylethylene	40.0 ± 10	20 ± 1.8
	Weight average	23.	

^a $k_1 = k_1 / (\text{number of active H atoms})$. ^b We consider only the axial hydrogens as reactive, consequently there are only 2 reactive C-H's in this molecule.

in toluene, the xylenes and mesitylene remains essentially constant, the slight increase in *p*-xylene reactivity resembling observations of Williams, *et al.*^{2b} This constancy of reactivity provides a strong argument for the validity of the whole kinetic scheme on which is based the derivation of the

expression used in calculating k_1/k_2 . Indeed, this scheme is upheld by all the data presented in Table III, which show that $k_{1,HR}/k_{1,toluene}$ remains constant whether stilbene or 1,1-diphenyl ethylene is used in its determination. This statement may be put in an alternative form, namely, that k_2 diphenylethylene/ k_2 stilbene is independent of solvent, as required by the proposed kinetic scheme. This is in spite of the about 20 fold greater reactivity of 1,1-diphenylethylene than stilbene, as shown by the data listed in Table IV.

TABLE IV

THE REACTIVITY OF 1,1-DIPHENYL ETHYLENE COMPARED WITH THAT OF STILBENE

Solvent	$k_{2,1,1\text{-diphenyl ethylene}}/k_{2,\text{stilbene}}$ based on	
	CH ₄ /CO ₂	CH ₄
Toluene	17.8	16.7
<i>o</i> -Xylene	17.1	15.6(?)
<i>m</i> -Xylene	22.0	21.6
<i>p</i> -Xylene	19.3	15.1(?)
Mesitylene	21.2	20.0
Ethylbenzene	19.3	18.4
Cumene	20.2	16.6
Indan	19.2	17.6
Average	19.5	18.6

Further inspection of the data given in Table III shows the considerable increase in the reactivity of a C-H bond as its character changes from a primary to a secondary and to a tertiary. This is a well known fact reported by many investigators, see *e.g.* Table V and the data published by Steacie.⁶ It is also gratifying to see the excellent agreement between the data given in Table III and similar data, obtained in this Laboratory by a different method, for a series of alkylated naphthalenes.⁷ In both series the secondary C-H is four times as reactive towards methyl radicals as the primary C-H. Actually, even the absolute values of k' for toluene and the other methylated benzenes differ only insignificantly from those observed for methylated naphthalenes. The rate constants k_1 determined by the method used in this study contain a contribution from the respective rate constants of addition to the solvent,⁴ *i.e.* " k_1 " computed = "true" k_1 + respective k_2 of the solvent. In the case of toluene the latter term contributes only about 10% to the observed rate constant, and its contribution is substantially lower for the other investigated hydrocarbons. Consequently, no attempt was made to introduce the appropriate corrections.

Table V shows how the data reported in this paper compared with those obtained for reactions involving ROO·, *t*-BuO·, CCl₃· and polystyryl radicals. The agreement between the respective relative rate constants of abstraction is remarkable in view of the vastly different nature of the abstracting radicals. The agreement with Urry's values, concerned with the same system as ours although obtained at a slightly different temperature, call for a special attention.

(6) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Co., New York, N. Y., 1956.

(7) J. Gresser, J. H. Binks and M. Szwarc, THIS JOURNAL, **81**, 5004 (1959).

TABLE V

RELATIVE RATE CONSTANTS OF H ABSTRACTION BY RADICALS PER ACTIVE H ATOM

Rate constant per active H of toluene taken as unity

Radical Hydrocarbon	ROO· ^a $T = 90^\circ$	CCl ₃ · ^b $T = 91.5$	Poly-styryl $T = 100^\circ$	<i>t</i> -BuO· ^c $T = 135^\circ$	CH ₃ · ^d $T = 80^\circ$	CH ₃ · ^e $T = 65^\circ$
Toluene	1.00	1.00	1.00	1.00	1.00	1.00
<i>o</i> -Xylene	1.20	...	0.99
<i>m</i> -Xylene	1.15	1.00	..	1.25	...	1.00
<i>p</i> -Xylene	1.6	1.13	..	1.52	...	1.19
Mesitylene	1.9	1.00	..	1.22	...	0.94
Ethyl benzene	7.75	4.6	3.7	3.2	3.5	4.14
Cumene	13.3	12.5	9.0	5.1	10	12.9
Indan	37	7.1	8.3
Tetralin ^f	134	25.6	..	15.2	...	23
Diphenyl methane	16	11.9	9.5

^a G. A. Russell, THIS JOURNAL, **78**, 1047 (1956). ^b C. Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951). ^c A. L. Williams, E. A. Oberright and J. W. Brooks, THIS JOURNAL, **78**, 1190 (1956). ^d W. H. Urry, Abstract of paper read in Org. Chem. Symp. Denver, June 1950. ^e This work. ^f We consider only the axial hydrogens as reactive, consequently, there are only 2 reactive C-H's in tetralin.

The increase in the reactivity in the series ethyl benzene, indan and tetralin is upheld convincing us of the reality of this phenomenon. However, the explanation of this trend proposed by Russell²² is not sufficient. Russell argues that no strain exists either in the initial or in the transition state of the reaction involving tetralin, while this strain increases in the reaction involving indan. This makes the former molecule more reactive than the latter in accordance with the observation. However, such an explanation would call for a decrease in the reactivity of indan if compared with that of ethylbenzene, and the latter should show a similar reactivity to tetralin. Actually, both indan and tetralin are substantially more reactive than ethylbenzene.

Inspection of models leads to interesting conclusions. It is expected that in the transition state the abstracted α hydrogen atom is directed perpendicularly (axially) to the plane of the benzene ring to permit the system to gain the resonance energy of the eventually formed benzyl radical. However, if this is done a considerable strain (\gg 8 kcal./mole) results from the repulsion between the closest β hydrogen and the ortho hydrogen of the ring. (This value, as well as the other values given here, were calculated by using potential energy of non-bonded H atoms given by Mason and Kreevoy.⁸) The repulsion can be decreased by abandoning the staggered conformation of α and β hydrogens and by bringing two β hydrogens to an equal distance from the ortho hydrogen. This reduces the strain energy between those hydrogens and the aromatic hydrogen to about 6 kcal./mole and increases the torsional energy of the α - β C-C bond by about 1 kcal./mole, bringing the total strain energy to about 7 kcal./mole. Since the least strained conformation of ethylbenzene, in which the α - β C-C bond is axial, leaves still about 4 kcal./mole of strain energy, the proposed conformation of the transition state would add approximately 3 kcal./mole to the activation energy of the abstraction process. Consequently, the abstraction prob-

(8) E. A. Mason and M. M. Kreevoy, *ibid.*, **77**, 5805 (1955).

ably takes place in a somewhat skewed conformation leading to some loss in the resonance of the transition state. In the extreme case, if the C-CH₃ bond is axial which removes the strain in the transition state, the C-H bond is inclined by about 50° to the plane of benzene ring. Assuming that the change of resonance energy with the angle of inclination is given by a cos. function and that only one half of the resonance energy of benzyl radical is gained in the transition state, one calculates the loss in the resonance energy to be about 4 kcal./mole.

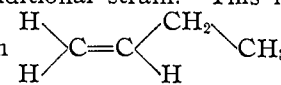
We conclude, therefore, that due to these factors the α C-H bonds in ethyl benzene are *less* reactive than anticipated, while the axial C-H bonds of tetralin should represent the "normal" secondary α C-H bonds since no further strain is involved in attainment of the respective transition state. This means that only the two axial α C-H bonds of tetralin are considered as the most reactive, see Tables III and V, while in indan all 4 α C-H's are equally reactive.

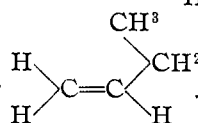
It is interesting to compare these results with those of Trotman-Dickenson and Steacie.⁹ Using their data and assuming constant frequency factors, we calculate the ratio of the rate constants of H abstraction for primary to secondary aliphatic C-H's at 65° to be 1:16. This is close to the ratio 1:23 observed for the pair toluene-tetralin but very different from the ratio 1:4 found for the pair toluene-ethylbenzene. The problem of the direction does not arise in the aliphatic series, and hence the same ratio of the rate constants of abstractions from primary and secondary C-H's might be anticipated in both series if "normal" C-H bonds are considered. Of course, the respective absolute values for C-H's α to benzene ring must be correspondingly lower than those characterizing the aliphatic C-H's because of the additional gain in the resonance energy of the transition state.

Extending these ideas to reactions involving cumene, we notice that the axial direction of α C-H bond leads to an even larger strain in this compound than in ethylbenzene. The calculated total strain of this conformation amounts to 12 kcal./mole as compared with 8 kcal./mole for the C-H direction in the plane of benzene ring. Consequently, even greater loss of resonance energy is expected in the relevant transition state, and that accounts well for the low ratio of the respective rate constants.

It is instructive to discuss the results obtained for the series of C-H's α to benzene ring with those obtained for the series of C-H's α to C=C double bond. The results for the latter series obtained in our Laboratory⁴ agree well with those of Trotman-Dickenson and Steacie⁹ if computed on the basis of constant frequency factor (see Szwarc and Binks¹⁰). Now, the ratio of the rate constants for the abstraction from primary and secondary C-H's is larger in this series, being about 1:10 (see ref. 10), than in the aromatic series. Inspection of the relevant

models reveals that butene-1 may acquire the α C-H axial conformation suffering only about 1 kcal./mole of additional strain. This is true for

the conformation 

for . The configuration round α

carbon is still tetrahedral. Hence, this ratio should be only slightly smaller than that found for the aliphatic series, in accord with observations. However, a considerable strain is developed in the transition state of 3-methylbutene-1, and consequently the ratio C-H secondary to C-H tertiary approaches that found for the pair ethylbenzene-cumene and is considerably lower from the ratio observed in the aliphatic series.

Steric inhibition of resonance in the transition state was observed for substituted aromatic compounds. For example, photochemical or peroxide induced chlorination of 2,3,4,5,6-pentachloroethylbenzene proceeds to a great extent on the β carbon.¹¹ Even more clear cut examples are provided by the work of Kooyman¹² on abstraction of H atoms by CCl₃ radicals. The rate of primary H to tertiary H abstraction from *p*- and *m*-methylisopropylbenzene was comparable to that calculated from the respective reactivities of cumene and toluene, but a one-fifth lower value was observed for *o*-methylisopropylbenzene. The present work indicates that the effects observed by Kooyman are also important in non-substituted aromatic derivatives.

Finally, we would like to discuss some points which emerge from inspection of Table IV. The investigated ratio $k_{2,\text{diphenylethylene}}/k_{2,\text{stilbene}}$ seems to be more reproducible if calculated on the basis of CH₄/CO₂ than if computed from the CH₄ only. Apparently, minor fluctuations in experimental conditions affect the absolute amount of methane formed but leave unaffected the CH₄/CO₂ ratio as is reasonable. Moreover, the $k_{2,\text{diphenylethylene}}/k_{2,\text{stilbene}}$ seems to be slightly larger if calculated on the basis of CH₄/CO₂. On checking our primary data we noticed that the amount of CO₂ formed in the presence of stilbene is often slightly lower than the amount formed in the "blank." The deviation is particularly noticeable at higher stilbene concentration. On the other hand, this effect is not noticed in experiments involving 1,1-diphenylethylene. The decomposition of acetyl peroxide forms primarily acetate radicals (CH₃CO₂·), and although their decarboxylation is exothermic,¹³ it was suggested that their decomposition needs a small activation energy.¹⁴ It seems that the hydrogen abstraction by acetate radicals is too slow to compete effectively with their decarboxylation. On the other hand, their addition to the C=C double bond is likely to be more rapid, and if the respective substrate is at

(9) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(10) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry (Kekule Symposium)," Butterworth Publishing Co., London, 1959, p. 262.

(11) S. D. Ross, M. Markarian and M. Nazzewski, *THIS JOURNAL*, **71**, 396 (1949).

(12) E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 329 (1953).

(13) I. Jaffe, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

(14) M. Szwarc and L. Herk, *ibid.*, **29**, 438 (1958).

higher concentration than some acetate, radicals might be lost by such a reaction.¹⁵ This should affect the calculation of the k_2/k_1 based on the amount of CH_4 formed, making it apparently larger, but it would leave approximately unchanged the k_2/k_1 based on the CH_4/CO_2 ratio. The results presented in Table IV may be accounted for in this way.

We are indebted to the referee for drawing our
(15) H. J. Shine and J. R. Slagle, *THIS JOURNAL*, **81**, 6309 (1959).

attention to the paper presented in Cleveland by J. C. Martin at the recent (April, 1960) meeting of A.C.S. This worker claims that cyclohexene reacts *directly* with acetyl peroxide giving the corresponding cyclohexyl acetate radical. The finding of Shine and Slagle¹⁵ therefore could be accounted for in an alternative way. We feel, however, that the problem of acetate radicals addition needs further studies and we intend to look closer into this reaction.

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND]

Adsorption Studies on Raney Nickel

BY R. J. KOKES AND P. H. EMMETT

RECEIVED FEBRUARY 18, 1960

Chemisorption measurements at -195° for carbon monoxide on a W-6 Raney nickel catalyst degassed at 400° indicate that the catalyst surface consists of 20% metal and 80% non-metal. The adsorption of hydrogen on such a sample in the range -78 to 0° is in agreement with this interpretation. The average pore diameter of the Raney nickel catalyst was found to be 84 Å.

Raney nickel catalysts are used extensively for the hydrogenation of organic compounds. The high surface areas of these catalysts (50 to 120 $\text{m}^2/\text{g}.$)¹⁻³ and their relatively high resistance to sintering suggests that alumina and possibly alkali retained in the activation process may be stabilizing the structure by acting as promoters. To obtain some idea as to the fraction of the surface that might be covered with these promoters,⁴ we have now measured the chemisorption of carbon monoxide at -195° and the chemisorption of carbon dioxide at -78° . We also obtained an approximate value for the adsorption of hydrogen on a sample degassed at 400° . These results together with pore size measurements are being reported in the present note.

Experimental

The two samples used in the present studies were obtained from a batch of W-6 catalysts⁵ prepared by the modification used by Smith and co-workers⁶ and stored under distilled water for about 10 months prior to use.

The adsorption studies were carried out on a standard BET apparatus.⁷ All gas was purified in a manner consistent with common practice. Samples were cooled to -195° in the presence of helium and corrections for departure from ideality were made. The extrapolated liquid vapor pressure was used for P_0 in the isotherms with carbon dioxide.

Results

Adsorption isotherms with carbon monoxide and nitrogen were obtained at -195° ; those with carbon dioxide were obtained at -78° . Amounts of chemisorption were estimated in the traditional fashion⁴ by determining the physical plus chemical adsorption at the standard temperatures indi-

cated above, warming the sample to a higher temperature (-78° for nitrogen and carbon monoxide, 25° for carbon dioxide), evacuating for 1 hr. and then redetermining the amount of adsorption, presumably all physical, at the standard temperature.

To identify the various isotherms the following nomenclature has been adopted: CO(T) refers to carbon monoxide adsorption (at -195°) on the clean catalyst; CO(P) refers to adsorption at -195° (presumably physical) on a catalyst which had been exposed to carbon monoxide at -195° and evacuated for 1 hr. at -78° ; N(OT) refers to nitrogen adsorption on top of a layer of chemisorbed carbon monoxide, *i.e.*, on a catalyst exposed to carbon monoxide at -195° and evacuated 1 hr. at -78° . The symbols $\text{CO}_2(\text{T})$ and $\text{CO}_2(\text{P})$ have the same significance, *mutatis mutandis*.

TABLE I
ADSORPTION ON DEGASSED W-6^a CATALYST

	Sample A (cc./g.)	Sample B (cc./g.)
$V_m \text{ N(T)}$	19.7	21
$V_m \text{ N(P)}$	19.7	..
$V_m \text{ N(OT)}$	19.5	19.1
$V_m \text{ CO}_2(\text{T})$..	18.4
$V_m \text{ CO}_2(\text{P})$..	18.4
$V_m (\text{CO})\text{T}^c$	24.2	25.4
$V_m (\text{CO})\text{P}$	20.8	21
Carbon monoxide chemisorp- tion CO(T) - N(OT)	4.7 (19%) ^b	6.3 (24%) ^b

^a See text for definitions. ^b These figures are the calculated % coverage of the catalyst with chemisorbed carbon monoxide provided the value to the left is a valid measure of chemisorbed carbon monoxide and this has a cross sectional area of 13 Å.² per molecule. This method for estimation has been used since part of the chemically adsorbed carbon monoxide may be removed by evacuation at -78° .⁸ ^c This is the amount of carbon monoxide adsorbed at the P/P_0 value corresponding to $V_m \text{ N(OT)}$.

- (1) G. W. Watt, *THIS JOURNAL*, **73**, 5791 (1951).
- (2) H. A. Smith, W. C. Bedoit and J. F. Fuzek, *ibid.*, **71**, 3769 (1949).
- (3) R. J. Kokes and P. H. Emmett, *ibid.*, **81**, 5032 (1959).
- (4) P. H. Emmett and S. Brunauer, *ibid.*, **59**, 310, 1553 (1937).
- (5) H. Adkins and H. Billica, *ibid.*, **70**, 695 (1948).
- (6) H. A. Smith, A. J. Chadwell and S. S. Kirdis, *J. Phys. Chem.*, **59**, 820 (1955).
- (7) P. H. Emmett, "Catalysis," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, Chapter 2.

- (8) R. J. Kokes and P. H. Emmett, *THIS JOURNAL*, **82**, 1037 (1960).