concentrations of the solvents, two possibilities can be discarded at once: deviations from random mixing due to large polymer–penetrant interaction, and non-uniform distribution of polymer segments at large v_1, as discussed by Flory and Krigbaum.[8] The former cannot be important for χ_1 less than unity (free energy of contact formation less than kT), while the latter would produce a change in χ_1 only at values of v_1 much higher than 0.7. As pointed out by Flory and Krigbaum[17] the assumption, fundamental in the derivation of equation (1), of a concentration independent lattice structure for the polymer–penetrant mixture, is probably not always valid. In general, therefore, one may expect the coördination number z to vary with composition, which will, of course, lead to a more complex formula than equation (1). In this connection it might be useful to examine the assumption, made in calculating v_1, that there is no volume change on mixing polymer and penetrant; if the lattice does indeed depend on the penetrant concentration, one might find some difference between the partial molar volumes in the mixture and the molar volumes of the pure components.

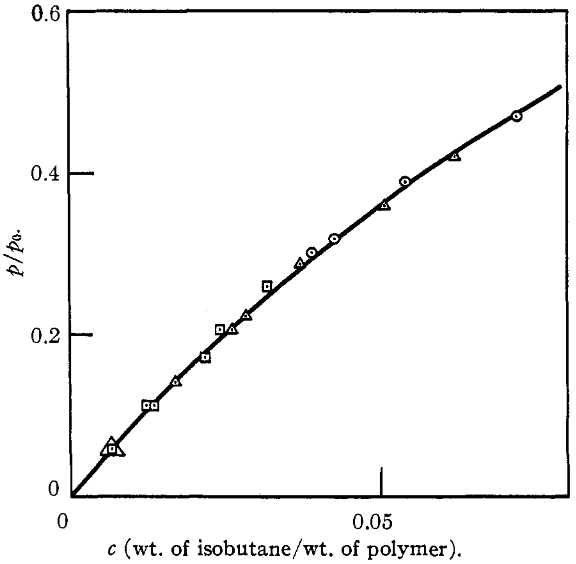

Fig. 1.—Sorption isotherms for isobutane with polyisobutylene: ⊙, 25°; △, 35°; ⊡, 45°.

The authors wish to express their gratitude to Professor P. J. Flory for helpful discussion and to Army Ordnance for support of the work.

ITHACA, N. Y.

[17] P. J. Flory and W. R. Krigbaum, "Ann. Review of Physical Chemistry," Vol. 2, Annual Reviews, Inc., Stanford, Cal., 1951, p. 383.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEXAS TECHNOLOGICAL COLLEGE]

Electric Moments of Some Methyl Ketones[1]

BY GEORGE K. ESTOK AND JOHN H. SIKES

RECEIVED JANUARY 9, 1953

Electric moments have been determined in benzene and dioxane solutions for four aliphatic unsaturated methyl ketones. The observed moments are interpreted in terms of resonance, methyl hyperconjugation, preferred configurations and solvent effects. Steric effects appear to favor the s-*cis* configuration when no hydrogen is present on the beta carbon. Moments for ethyl methyl ketone and isopropyl methyl ketone were also determined.

The influence of alpha-methyl group hyperconjugation in reducing the electric moments of certain unsaturated aldehydes and nitriles through the generation of hyperconjugated resonance structures in opposition to the primary moments has been discussed by Smyth.[2]

The influence of solvent on contribution of polar resonance structures in the case of anilines substituted in the para positions by electron withdrawing groups has been reported for dioxane solutions, which yielded higher apparent moments than benzene solutions.[3] Increased contributions from polar structures in dioxane were attributed to stabilization by hydrogen bonding, *i.e.*, $OC_4H_8O \ldots H_2\overset{+}{N}{=}C_6H_4{=}C{=}N^-$.

The compounds chosen for this investigation were mostly unsaturated methyl ketones with methyl groups in several positions subject to hyperconjugation. Determinations were made in benzene and dioxane solutions to observe the influences of resonance, methyl hyperconjugation, favored configurations, and solvents.

Experimental

Preparation and Purification of Compounds.—Boiling points reported for compounds have been corrected to 760 mm.

Mesityl oxide, an Eastman Kodak Co. White Label product was carefully fractionated through a metal helix packed column at reduced pressure; b.p. 129°, n^{25}D 1.4438, d^{25}_4 0.8597.

Methylmesityl oxide (3,4-dimethyl-3-penten-2-one) was obtained at an earlier date by careful fractionation from the several products obtained by the acetylation of trimethylethylene with acetic anhydride in the presence of anhydrous zinc chloride.[4] The compound was purified again by careful fractionation at reduced pressure just prior to use; b.p. 149°, n^{25}D 1.4500, d^{25}_4 0.8704.

Isopropenyl methyl ketone was prepared by deaminating the product formed by the reaction of ethyl methyl ketone, formaldehyde and dimethylamine hydrochloride, as reported by Hagemeyer[5]; b.p. 98°, n^{25}D 1.4212.

3,4-Dimethyl-4-penten-2-one was obtained as one of the products from the same reaction which produced methylmesityl oxide, and was similarly purified; b.p. 131°, n^{25}D 1.4230, d^{25}_4 0.8406.

Ethyl methyl ketone, b.p. 79.5°, n^{25}D 1.3774, d^{25}_4 0.8023, and **isopropyl methyl ketone**, b.p. 94°, n^{25}D 1.3860, d^{25}_4

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[1] Presented at the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December 4–6, 1952.

[2] R. E. Burk and O. Grummitt, Editors, "Chemical Architecture," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 23–51.

[3] C. Curran and G. K. Estok, THIS JOURNAL, **72**, 4575 (1950).

[4] G. Estok, M.S. Thesis, The Pennsylvania State College, 1947.

[5] H. J. Hagemeyer, Jr., THIS JOURNAL, **71**, 1119 (1949).

TABLE I

SLOPE–INTERCEPT DATA, POLARIZATIONS AND ELECTRIC MOMENTS (25°)

(Benzene, ϵ = 2.273, d = 0.873; dioxane, ϵ = 2.21, d = 1.028)

Solute	Solvent	$\frac{\Delta(\Delta\epsilon/w_2)}{\Delta w_2}$	$(\Delta\epsilon/w_2)_\infty$	$\frac{\Delta(\Delta d/w_2)}{\Delta w_2}$	$(\Delta d/w_2)_\infty$	$P_{2\infty}$	MR_D	μ
Mesityl oxide	Benzene	5.5	8.45	0.22	−0.036	191.0	(30.08)	2.79
	Dioxane	5.6	10.07	.00	− .220	195.8		2.83
Methylmesityl oxide	Benzene	3.4	7.91	.021	− .008	205.7	(34.62)	2.88
	Dioxane	3.5	9.32	.10	− .200	209.3		2.91
Isopropenyl methyl ketone	Benzene	6.9	9.48	.065	− .036	179.7	(25.05)[8]	2.74
	Dioxane	5.9	11.47	.00	− .216	186.5		2.80
3,4-Dimethyl-4-penten-2-one	Benzene	1.0	6.14	.032	− .044	169.9	(33.99)	2.56
	Dioxane	6.4	7.12	− .06	− .232	169.7		2.56
Ethyl methyl ketone	Benzene	4.3	11.18	− .08	− .074	177.9	(20.69)	2.76
	Dioxane	3.8	13.44	− .08	− .280	184.6		2.82
Isopropyl methyl ketone	Benzene	5.4	9.28	.034	− .083	182.6	(25.29)	2.76

0.8000, were Eastman Kodak Co. products, and were purified by careful fractionation.

Benzene and dioxane were purified as indicated in earlier work.[6]

Measurements and Calculations.—Measurements of *dielectric constants* and *densities* were carried out as previously described[6] except a dielectric cell of approximately 100 mmfd. with concentric nickel plates, manufactured by J. C. Balsbaugh, Cambridge, Mass., was used. Inlet and outlet tubes were attached for convenience. *Polarizations* at infinite dilution were calculated by the method of Hedestrand as modified by LeFevre and Vine.[7] Where the ratios of $\Delta\epsilon$ to weight fraction were not linear functions of concentration the solution values were extrapolated to infinite dilution. *Moments* in Debye units were calculated from the relation: $\mu = 0.221(P_{2\infty} - 1.05\ MR_D)^{1/2}$. *Molar refractions* listed in Table I were obtained from the densities and refractive indices of the purified compounds, except that for isopropenyl methyl ketone the refraction data reported by Brant[8] were used.

Discussion of Results

Where moments are hereinafter indicated without reference to method or solvent, values in benzene solution are understood.

The moment of 2.79 for mesityl oxide is only slightly higher than the average moment of about 2.75 for saturated aliphatic methyl ketones, and considerably lower than that for methyl vinyl ketone, 2.98.[9] A value of 2.84 has been previously reported for mesityl oxide,[10] but treatment of the data by the method of this work yields 2.81.

The low moment of mesityl oxide is attributed to the predominance of the s-*cis* (single-bond *cis*)[11] preferred configuration of the molecule. Fisher–Hirschfelder models reveal that steric hindrance and repulsion exist between methyl groups in the s-*trans* configuration, in which form polar resonance structures such as $H^+CH_2{=}C(CH_3)CH{=}C(CH_3)\text{-}O^-$ would greatly augment the primary carbonyl moment. Thus in an analogous case *trans*-crotonaldehyde, with no hindering beta-methyl group, yields 3.54 (in CCl_4) as compared to 2.90 for acrolein.[10] In the s-*cis* configuration for mesityl oxide, however, the polar resonance structures contribute little to the total moment.

The influence of an alpha-methyl group in conjunction with the s-*trans* configuration causes a reduction in moment. Thus methacrolein, 2.72, methacrylonitrile, 2.69 (gas), and α-methylcrotonaldehyde (tiglaldehyde), 3.39, have lower moments than acrolein, 2.90, acrylonitrile, 3.88 (gas), and *trans*-crotonaldehyde, 3.54 (in CCl_4), respectively.[9,10] This is attributed to the moment set up by alpha-methyl hyperconjugation in opposition to the primary moment.

When no hydrogen is present on the beta-carbon the s-*cis* configuration is favored, and the alpha-methyl hyperconjugation leads to an augmentation of the primary moment. This is well illustrated by the higher value of 2.88 obtained for methylmesityl oxide as compared to 2.79 for mesityl oxide itself.

The s-*trans*-configuration may be expected to predominate for isopropenyl methyl ketone, and the value of 2.74 illustrates how the augmenting (conjugation) and opposing (hyperconjugation) effects cancel to yield a moment essentially equivalent to that for isopropyl methyl ketone. Some doubt may accrue to the value of 2.74, however, because of the reported instability of isopropenyl methyl ketone[8]; however the index of refraction of this material did not change appreciably in two days, and a satisfactory boiling point was determined almost a month later.

The low moment of 2.56 for the non-conjugated case of 3,4-dimethyl-4-penten-2-one shows the effect of an isolated methylene group with hyperconjugation in opposition to the primary moment, and confirms the sense of the moment of a group analogous to that in isobutylene.

The moments determined in dioxane solutions lead to the same general configurational conclusions as those studied in benzene. The dioxane data indicate only a small solvent effect tending to increase apparent moment by about 0.05 *D* whether the ketone is unsaturated or not. There is no definite evidence that dioxane stabilizes hyperconjugated structures by electrostatic interaction; however, the compounds studied have been revealed to have structures such as would not be suitable for the observation of such an effect. The exception would be the non-conjugated case, for which the identical moments obtained might

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(6) J. Moede and C. Curran, THIS JOURNAL, **71**, 852 (1949).

(7) R. J. W. LeFevre and H. Vine, *J. Chem. Soc.*, 1805 (1937).

(8) J. H. Brant, THIS JOURNAL, **64**, 2224 (1942).

(9) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Mass. Inst. of Technology, Cambridge, Mass., 1948.

(10) J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

(11) R. S. Mulliken, *Rev. Modern Phys.*, **14**, 265 (1942).

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

RECEIVED SEPTEMBER 3, 1952

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.