Fig. 1.—Relative volume–temperature curves: curve A for polymethylene O; curve B for polyethylene △.

demonstrated[5,8,9] that to obtain reliable values of T_m in polymers, the heating in the vicinity of the melting temperature must be gradual and should occur over a period of several days. Other observers[10,11] have reported the decomposition of polymethylene around 300° without noting any indication of melting at lower temperatures. If visual methods were employed, the true melting point was probably obscured by the very high viscosity of the polymer. Both the branched and linear polymers supercool, the amount of supercooling, of course, depending on the cooling rate.

Experimental.—Polymethylene was prepared according to the method described by Buckley and Ray[10] by means of the decomposition of diazomethane, using trimethyl borate as catalyst. The infrared absorption spectrum of thin films of the polymer was identical with that reported by these authors,[10] indicating the absence of methyl groups and hence a linear molecule. Its intrinsic viscosity in units of 100 ml./g., was 8.6 ± 0.1, in freshly distilled xylene at 100°, so that our polymer is of high molecular weight.[3] The polyethylene was obtained from the Bakelite Corporation and is designated as DYNH resin. Its physical properties have been described in the literature.[3]

The dilatometric samples were films approximately 0.2–0.3 mm. thick prepared from a 1% xylene solution held at 110° in an atmosphere of nitrogen at reduced pressure. After the bulk of the solvent was removed, the films were dried in vacuo at 70° for 28 hours. The dilatometric procedure, using mercury as a confining fluid, has been described previously.[8] Observations were made in the order of ascending temperature and in the melting region, the temperature was raised only 1° per 24 hours. A considerable amount of recrystallization, as has been observed in other polymers,[5,8,9] occurred.

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(8) P. J. Flory, L. Mandelkern and H. K. Hall, ibid., **73**, 2352 (1951).

(9) L. Mandelkern, R. R. Garrett and P. J. Flory, ibid., **74**, 3949 (1952).

(10) G. D. Buckley and N. H. Ray, J. Chem. Soc., 3701 (1952).

(11) H. Meerwein, Angew. Chem., **60**, 78 (1948).

cis- and trans-Propenylbenzene and their Azeotropes with n-Decane

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Samples of pure cis- and trans-propenylbenzene were desired during the course of two independent investigations in these laboratories. The propenylbenzenes were needed as spectral standards for the infrared spectrographic analyses of olefins resulting from solvolysis of 2-phenyl-1-propyl and 1-phenyl-2-propyl p-bromobenzenesulfonates. They were also desired for testing azeotrope-formation with n-decane. These azeotropes were found during the distillation of the products from the reactions of sodium allylbenzene in pentane with methanol and various halides.[2]

Attempts to separate the pure cis-isomer from the propenylbenzenes obtained by isomerization of allylbenzene[3] were unsuccessful even though columns of ca. 100 theoretical plates were used. The propenylbenzene obtained in this manner was predominantly the trans-isomer.[4] Catalytic hydrogenation of 1-phenyl-1-propyne gave the cis-propenylbenzene which was satisfactorily purified by a precision distillation through a 112-theoretical-plate center-rod column. The trans-propenylbenzene was obtained without difficulty and free of the cis-isomer from the methanolysis of sodium allylbenzene in pentane. The small amount of the cis-isomer found in this reaction presumably was separated as the n-decane azeotrope.

TABLE I

Physical Properties and Ultraviolet Absorption Maxima of cis- and trans-Propenylbenzene

Isomer	cis	trans
B.p., °C. (20 mm.)	64.5	73.5
$n^{25}D$	1.5400	1.5473
d^{25}_4	0.9107	0.9019
MR_D, calcd.	39.69	39.69
found	40.69	41.56
exaltation	1.00	1.87

Ultraviolet absorption maxima in 95% ethanol

λ, mμ	ϵ_m	λ, mμ	ϵ_m
240.6	13800	250	17300
279	Shoulder	284	1100
290	120	293	780

The physical and optical properties of the cis- and trans-propenylbenzenes (Table I) clearly show the effects of steric inhibition of resonance in the cis-isomer due to interference between the ortho-hydrogen of the benzene ring and the methyl hydrogens in the side chain. This produces a reduction of 0.87 in the exaltation of the molecular refraction, and similar reductions are displayed by

(1) (a) Standard Oil Company of California Fellow in Chemistry 1950–1952; (b) research supported by Office of Naval Research.

(2) The results of these investigations are reported elsewhere.

(3) M. Tiffeneau, Comp. rend., **139**, 482 (1904).

(4) The Am. Pet. Inst., "Selected Values of Properties of Hydrocarbons," Vol. III, Table 13p gives the following free energies of formation ($\Delta F°_{ig}$ kcal.): cis-propenylbenzene, 51.84 and trans-propenylbenzene 51.08. From these values, the composition of the thermal equilibrium mixture is estimated to be 21.7% cis- and 78.3% trans-propenylbenzene.

Table II

MOLAR REFRACTIONS AND EXALTATIONS FOR VARIOUS STYRENES

$$\underset{R_1}{\overset{C_6H_5}{\diagdown}}C{=}C\underset{R_3}{\overset{R_2}{\diagup}}$$

R₁	R₂	R₃	MRD	Exaltation	Ref.
H	H	H	36.44	1.37	5
Me	H	H	40.63	0.94	5
H	Me	H	40.70	1.00	a
H	H	Me	41.57	1.87	a
Me	Me	H	45.14	0.83	6
Me	H	Me	45.02	0.70	6
Me	Me	Me	49.62	0.59	7

a This work.

various substituted styrenes (Table II). The values in Table II illustrate the reductions of molecular refraction due to the placement of a β-group *cis* to phenyl rather than *trans* to it, and due to an α-methyl group, especially when it is *cis* to the β-methyl group.[8]

The physical properties for the propenylbenzene now in the literature[5,9] appear to be mainly those for the *trans*-propenylbenzene.

The infrared spectra of the propenylbenzenes (Table III) contain several features which lend strong support to the correctness of the *cis*-,*trans*-assignment. A band at 1412 cm.⁻¹ of medium intensity, characteristic of the hydrogen in plane deformation of *cis*-disubstituted ethylenes,[10] appears only in the spectrum of the *cis*-propenylbenzene. The corresponding band in the *trans*-substituted molecules is usually weak and occurs at about 1300 cm.⁻¹. Such a band is found at 1309 cm.⁻¹ for the *trans*-compound. One of the most characteristic

Table III

PRINCIPAL INFRARED ABSORPTION BANDS OF *cis*- AND *trans*-PROPENYLBENZENES

s = strong, m = medium, and w = weak intensities.

Frequency, cm.⁻¹

cis	trans	cis	trans
702 s	694 s	1445 s	1445 s
	736 s	1495 s	1495 s
769 s		1582 w	1582 w
808 s	812 s	1608 m	1608 m
917 s	912 m		1650 w
939 m	948 s	1653 w	1667 m
	962 s	1721 w	1779 w
971 w	980 s	1815 w	1799 w
1034 m	1034 m	1887 w	1887 w
1073 w	1073 m	1953 w	1957 w
1087 m		2924 m	2924 m
1190 w	1183 w	2976 s	2959 s
	1309 w	3067 s	3067 s
1372 s	1382 m	3106 s	3106 s
1412 m			

(5) Am. Pet. Inst. "Selected Values of Properties of Hydrocarbons," Table 13a,b.

(6) D. J. Cram, THIS JOURNAL, 71, 3883 (1949).

(7) K. von Auwers and F. Eisenlohr, J. prakt. Chem., [2] 84, 32 (1911).

(8) Styrene to α-methylstyrene gives a reduction of 0.43 and *trans*-propenylbenzene to *cis*-2-phenyl-2-butene gives a reduction of 1.17.

(9) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946, p. 191.

(10) N. Sheppard and D. M. Simpson, Quart. Rev., 6, 1 (1952).

bands in the infrared spectra of disubstituted ethylenes corresponds to the asymmetrical out-of-plane hydrogen deformations. These are found at around 965 cm.⁻¹ in the *trans*-molecules and in the *cis*-compounds from 690 to 820 cm.⁻¹.[10,11] The spectrum of *trans*-propenylbenzene shows a strong band at 962 cm.⁻¹ while there is no such strong band for the *cis*-compound in the same vicinity. The corresponding vibration of the *cis*-propenylbenzene may correspond to the strong band at 769 cm.⁻¹.[12] The lowering of the C=C stretching frequencies from 1667 to 1653 cm.⁻¹ in going from *trans*- to *cis*-propenylbenzene agrees well with an average shift of 17 cm.⁻¹ in the same direction observed for a series of *cis*- and *trans*-olefins.[10] The published[13] infrared spectrum of propenylbenzene (β-methylstyrene) agrees well with our spectrum for the *trans*-isomer except in the region around 1667 cm.⁻¹.

The azeotropes of the propenylbenzenes with *n*-decane were first discovered by an adsorption–displacement analysis using silica gel as the adsorbent and methanol as the desorber, and they were confirmed by distillation of synthetic mixtures. The *trans*-propenylbenzene azeotrope was obtained as a constant-boiling and constant-refractive index series of cuts. There is some doubt that the *n*-decane–*cis*-propenylbenzene mixtures formed an azeotrope as the boiling points of the mixture and *cis*-propenylbenzene were virtually the same by our temperature instrumentation. There was a small but definite plateau in the refractive index curve. This work could not be repeated with larger quantities because of the limited amount of *cis*-propenylbenzene available. Table IV contains the physical properties and composition of the *n*-decane–*trans*-propenylbenzene azeotrope along with the corresponding approximate values for the *n*-decane–*cis*-propenylbenzene azeotrope.

Table IV

PHYSICAL PROPERTIES OF THE *n*-DECANE AZEOTROPES WITH *cis*- AND *trans*-PROPENYLBENZENE

Isomer	cis	trans
B.p., °C. (20 mm.)	64.5	70
n^{25}D	1.510	1.4553
Composition (by wt.)		
n-Decane, %	*ca.* 19	60.8
Propenylbenzene, %	*ca.* 81	39.2

Experimental Part[14]

cis-Propenylbenzene.—1-Phenyl-1-propyne[15] (28.0 g.) was hydrogenated at atmospheric pressure in 300 ml. of dry ether with 2 g. of 5% palladium on Norite. After 4.5 hours, 6.1 liters of hydrogen had been taken up. The solution was filtered to remove the catalyst and the solvent was evaporated. The product was fractionated at atmospheric pressure through a center-rod column (112 theoretical plates) at a reflux ratio of 200:1. The center fractions (b.p. 168–169°, n^{25}D 1.5398) were carefully redistilled at 20 mm. pressure using a twisted, stainless steel wire-gauze

(11) G. B. B. M. Sutherland, Rec. Chem. Progress, 13, 79 (1952).

(12) Professor W. F. Edgell (in a private communication) and Referee I suggested this assignment. However, Sheppard and Simpson[10] and Sutherland[11] choose the region around 690 cm.⁻¹ for this vibration.

(13) Am. Pet. Inst. Infrared Spectrogram No. 330.

(14) All melting points and boiling points are uncorrected except where noted.

(15) K. N. Campbell and M. J. O'Connor, THIS JOURNAL, 61, 2897 (1939).

column,[16] 5 mm. × 30 in., equipped with an electrically heated jacket over a vacuum jacket. The physical properties and ultraviolet absorption maxima (using a Cary Model 11 PMS Spectrophotometer) are given in Table I and the principal infrared absorption bands (using a Beckman IR-2 Spectrophotometer) of the pure liquid in Table III.

trans-Propenylbenzene.—This material was obtained as a constant boiling, constant refractive index series of cuts from the distillation of the products from the reaction of sodium allylbenzene in pentane with methanol. The distillation was carried out at 20 mm. pressure in an analytical manner using the twisted wire gauze column described above. The physical properties and ultraviolet absorption maxima are given in Table I and the infrared absorption bands in Table III.

The 2,4-dinitrobenzenesulfenyl chloride derivative, m.p. 91.5–92°, was prepared[17] from another sample of *trans*-propenylbenzene, $n^{25}D$ 1.5468.

Anal. Calcd. for $C_{15}H_{13}SN_2ClO_4$: C, 51.06; H, 3.71. Found: C, 51.36; H, 3.87.

Azeotropes with *n*-Decane.—Synthetic mixtures of pure *n*-decane, $n^{25}D$ 1.4098, with *cis*-propenylbenzene and pure *n*-decane with *trans*-propenylbenzene were carefully distilled at 20 mm. pressure in the twisted wire-gauze column. Table IV contains the physical properties and compositions of the azeotropes. The compositions were determined by means of the non-linear, refractive index–composition curves which were based upon the indices of a number of synthetic mixtures.

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(16) J. R. Bower and L. M. Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

(17) D. L. Hagmann, Ph.D. Thesis, University of California, Los Angeles, 1950.

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Dynamic Structure of Oxide Cracking Catalyst

BY A. G. OBLAD, S. G. HINDIN AND G. A. MILLS

Recently, Milliken, Mills and Oblad[1] advanced the hypothesis that the catalytic activity of a silica–aluminum cracking catalyst depends for driving force upon the ability of the aluminum ion to undergo a reversible change in coördination number from six to four. This reversible shift in coördination of the aluminum would involve a movement of the oxygen ions of a few tenths of an ångström unit. The purpose of this note is to present experimental evidence that, at cracking conditions, the silica–alumina structure is extremely mobile in the presence of water and such a proposed coördination shift is easily possible.

The exchange of oxygen between water enriched in O^{18} and a silica–alumina cracking catalyst was measured under conditions which the catalyst experiences when used in cracking petroleum. Previous work on such water–oxide exchange[2,3] has been carried out primarily at relatively low temperatures, 100°, and for long times, up to one

(1) T. H. Milliken, G. A. Mills and A. G. Oblad, *Faraday Society Discussions*, **8**, 279 (1950); also Vol. III "Advances in Catalysis," Academic Press, Inc., New York, N. Y., 1951.

(2) G. A. Mills and S. G. Hindin, THIS JOURNAL, **72**, 5549 (1950).

(3) E. Whalley and E. R. S. Winter, *J. Chem. Soc.*, 1175 (1950).

month. In commercial cracking, temperatures are of the order of 450°. Working at these latter temperatures using a flow system, it was found that remarkably fast exchange occurs so that between 50 and 100% of *all* oxygen of the silica–alumina structure will undergo exchange within a 20-minute period.

Experimental

A flow system was used, employing conventional apparatus as for catalyst testing.[4] The silica–alumina catalyst was commercial pelleted Houdry Type S-45 previously described.[2] The procedure consisted of passing water enriched in O^{18}, at atmospheric pressure, at constant rate through the catalyst bed maintained at 450°, collecting the exit water in fractions, and measuring its O^{18} content by equilibrating with CO_2 which was then examined in a mass spectrometer. Experiments also were carried out in which oil was charged to the catalyst simultaneously with the water. In both sets of runs flow rates closely approximated those of commercial operation in which steam and oil are charged to the catalyst. Runs were for a 20-minute period, again conventional for cracking. Typical results are shown in Table I.

TABLE I

OXYGEN EXCHANGE BETWEEN WATER AND SILICA–ALUMINA AT 450°

Catalyst: Houdry Type S-45, 87.5% SiO_2–12.5% Al_2O_3, H_2O^{18}: 1.59 atom % O^{18}, normal isotopic concn., 0.20 atom % O^{18}.

Expt. no.	Flow period,[a] min.	Oxygen in catalyst, g.	Oxygen in water[a] Charged, g.	Col-lected, g.	O^{18} in water fraction, atom %	% Oxygen of oxide in equil. with added H_2O[d]
1	10	7.87	1.29		0.66	
	10		1.15		.91	Total 44
2	5	62.6	3.48	2.18	.21	
			3.02	2.65	.24	
			3.11	3.15	.39	
			3.73	3.75	.61	Total 67[b]
3[c]	20	62.6	13.3		.60	53

[a] Values are incremental, not total. [b] In this experiment, 15.0 g. of water was charged during the run—only 13.2 g. was recovered. Averaging the data on a no loss basis disproportionately weights the data toward higher values for % exchange, as is evident from column six. Assuming the 1.8 g. loss showed no exchange, we would arrive at a value of 67% of the oxide oxygen equilibrating. It is reasonable to assume some exchange however, and so the true value for % oxygen equilibrating will be greater than 67%. [c] During this experiment, light East Texas gas oil was simultaneously charged to the catalyst at 1.5 liquid hourly space velocity. [d] For method of calculation see reference 2.

In view of these data, several static experiments were carried out at 450° In these, catalyst and enriched water were sealed into an evacuated tube and heated at 450° for periods of 1.5 to 4.0 hours. Results in all cases indicated that *all* catalyst oxygen had equilibrated. Less exchange was reported previously (ref. 2, Table VIII). The reason for the lower results is not known, although less exchange may occur at the lower water vapor pressures used earlier.

Discussion

The data of Table I show that one-half or more of the catalyst oxygens exchange in a few minutes, a period in which the characteristic catalyst structure-area, pore-size distribution, does not alter measurably. For extensive loss of area to occur requires months of commercial operation. It should be noted that the figures indicate far more oxygens have exchanged than can be accounted for in the two uppermost surface layers—those together

(4) J. Alexander, *J. Proc. Am. Pet. Inst.*, **27** (III) 51, Nov. (1947).