of a catalyst fragment, an active hydrogen, or other material present as an impurity to give a saturated hydrocarbon end group.

The reaction of hexamethylenedithiol and dibenzalcyclohexanone also produces a polymer of low molecular weight. However, it was not possible to extend the reaction to include dimercaptan addition to 3,3'-dinitrodibenzalacetone, diethyl 1,7octadiene-1,8-dicarboxylate, 1,6-diphenyl-1,5-hexadiene-3,4-dione or dimethyl acetylenedicarboxylate.

Experimental

Preparation of Polymers from Dibenzalacetone and Hexamethylenedithiol.-A typical solution polymerization consisted of charging a four-ounce polymerization bottle with sisted of charging a four-ounce polymerization bottle with 1.981 g. (0.01349 mole) of hexamethylenedithiol and 3.088 g. (0.01348 mole) of dibenzalacetone in 15 ml. of dry ben-zene and adding 0.2 ml. of piperidine. The solution was pro-tected by a nitrogen atmosphere and the bottle was tumbled in a 30° constant temperature bath for 24 hours. The polymer was precipitated with 25 ml. of methanol, dried and means its total. The inherent wineseity as determined in reprecipitated. The inherent viscosity⁴ as determined in benzene was 0.31 at 25°.

Anal. Calcd.⁵ for $C_{23}H_{28}S_2O$: C, 71.82; H, 7.34; S, 16.68. Found: C, 72.06; H, 7.58; S, 16.56.

Polymers from Dibenzalcyclohexanone and Hexamethylenedithiol.—A polymer was produced from these monomers by the same general method as shown above. The inherent viscosity in benzene at 25° was 0.14.

Anal. Caled. for C₂₆H₃₂S₂O: C, 73.53; 15.10. Found: C, 73.95; H, 7.66; S, 14.38. 73.53; H, 7.60; S,

Attempted Oxidation of Polymer End Groups .-- To a solution of 1.015 g. of polymer from dibenzalacetone and hexamethylenedithiol (inherent viscosity 0.22) dissolved in 50 ml. of chloroform was added 0.1 g. of iodine. The solution was shaken at room temperature for 24 hours after which it was poured into a mixture of 100 ml. of methanol and 50 ml. of water containing 1 g. of sodium bisulfite. The polymer was isolated by decantation and was washed with two 100-ml. portions of methanol. The inherent viscosity was 0.06.

Effect of Monomer Balance.-The molar ratio of hexamethylenedithiol and dibenzalcyclohexanone in a typical polymerization was varied and the effect upon the viscosity of the polymer was noted. These experiments are recorded in Table I.

TABLE I

EFFECT OF MONOMER BALANCE ON INHERENT VISCOSITY OF POLYMER

Hexamethylene- dithiol, g.	Dibenzalcyclo- hexanone, g.	Molar ratio dithiol/ketone	Inherent viscosity
0.996	1.894	96/100	0.16
.990	1.863	97/100	.16
.991	1.846	98/100	. 19
.987	1.820	99/100	.21
.975	1.780	100/100	.23
.991	1.791	100/99	.24
.987	1.766	100/98	.20
1.002	1.774	100/97	.18
0.989	1.733	100/96	.15
1.000	1.734	100/95	.16

Time Required for Polymer Formation.-At 30° a solution of 0.0067 mole of hexamethylenedithiol and dibenzalacetone in 10 ml. of benzene was polymerized and the reaction followed by noting the viscosity and yield of the polymer. The polymers were dried *in vacuo* until there was no further loss of weight. The results are reported in Table II.

TABLE II

Notes

TIME REQUIRED FOR POLYMER FORMATION

TIME RESOLUTE FOR TOPIMER TORMATION					
Time, hr.	Inherent viscosity	Vield, %	Time, hr.	Inherent viscosity	Vield, %
0.005	0.12	12	1	0.27	82
.083	.21	48	2	.26	75
.167	.33	68	6	.25	80
.250	.34	76	9	.24	72
. 500	.29	71	24	.27	71
.750	.29	71	48	.20	71
			72	.21	54

Mercaptan Disappearance.-By amperometric titration⁶ the rate of disappearance of thiol end groups was followed in an emulsion polymerization.

These titrations showed that in the addition of hexamethylenedithiol to dibenzalacetone, the mercaptan groups disappeared very rapidly; nearly 70% in a minute, nearly 80% in seven minutes, 95% in an hour and 99% in twelve Thereafter there appeared to be no further dehours. crease in mercaptan groups and even possibly a slight increase.

(6) I. W. Kolthoff and W. E. Harris, Ind. Eng. Chem., Anal. Ed., 18 161 (1946).

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Equilibrium Sorption of Several Organic Diluents in Polyvinyl Acetate¹

BY R. J. KOKES, A. R. DIPIETRO AND F. A. LONG RECEIVED AUGUST 27, 1953

In the course of an investigation of the kinetics of vapor take-up by thin polymer films,² the equilibrium sorption has been determined for several organic diluents in polyvinyl acetate (viscosity average molecular weight approximately 170,000). Experiments have been made at 30, 40 and 50° with acetone, benzene and 1-propanol and at 40° with propyl chloride, allyl chloride, propylamine and isopropylamine. In all cases the solutions were concentrated in polymer; values of v_1 , the volume fraction of solvent, ranged from 0.02 to 0.20. In these experiments the diluent concentration in the swollen polymer in equilibrium with a given vapor pressure of diluent was determined gravimetrically using a quartz spiral balance. The procedure, apparatus, and materials used have been discussed in detail elsewhere.²⁻⁴ Results of the present experiments are summarized in Table I, which gives v_1^{5} as a function of p/p_0 , the ratio of diluent vapor pressure for the swollen polymer to that for the pure diluent. The systems studied, although polar, are relatively simple inasmuch as the polymer is non-crystalline and above its second-order transition temperature. It is of interest, therefore, to consider these data in the light of the Flory-Huggins^{6,7} theory of polymer solutions.

(1) Work supported by a grant from Office of Ordnance Research, U. S. Army.

R. J. Kokes and F. A. Long, submitted for publication.
S. Prager and F. A. Long, THIS JOURNAL, 73, 4072 (1951).

(4) R. J. Kokes, F. A. Long and J. L. Hoard, J. Chem. Phys., 20, 1711 (1952).

(5) The volume fractions were calculated from the experimentally determined weight fractions assuming that solvent and polymer volumes were additive on mixing.

(6) P. J. Flory, J. Chem. Phys., 10, 51 (1942).

⁽⁴⁾ We are indebted to Messrs. Donald Janssen and Norbert Goeckner for all inherent viscosities reported.

⁽⁵⁾ We are indebted to the Micro-Tech Laboratories, Skokie, Ill., and to Mr. Joseph Nemeth of the University of Illinois for the microanalytical results.

According to Flory, the relation between a_1 , the solvent activity, and v_1 is, for a polymer of infinite molecular weight

$$\ln a_1 = \ln v_1 + (1 - v_1) + \chi_1 (1 - v_1)^2 \qquad (1)$$

where χ_1 is the Flory-Huggins parameter (originally μ) characteristic of the particular system. Initially, χ_1 was regarded as a measure of the enthalpy of solution, but recent considerations⁸ suggest that χ_1 has the more general form

$$\chi_1(1-v_1)^2 = \frac{\Delta \overline{F}_1'}{RT} = \frac{\Delta \overline{H}_1}{RT} - \frac{\Delta \overline{S}_1'}{R}$$
(2)

where $\Delta \bar{F}'_1$ is the change in free energy, excluding

FLORY-HUGGINS INTERACTIONS PARAMETERS FOR DILUENTS WITH POLYVINYL ACETATE

Acetone, 50°			Benzene, 50°			
\$/\$0	V 1	χ1	\$/\$0		X1	
0.113	0.0296	0.39	0.185	0.0585	0.24	
.163	.0437	.39	.221	.0703	.25	
.198	.0543	. 39	.258		.26	
.251	.0714	.38	.295	.0955	.27	
. 305	.0900	. 37	. 332	.1111	.26	
	$\overline{\chi}_1 =$	0.38 ± 0.01		$\tilde{\chi}_1 =$	0.26 ± 0.04	
	Acetone	,40°	Benzene, 40°			
0.164	0.0448	0.37	0.212	0.0587	0. 39	
.242	.0682	.38	.249	.0763	. 30	
.290	.0874	. 34	.311	.0957	.34	
.355	. 1118	. 34		.1139		
. 447	. 1496	. 34		$\overline{\chi}_1 =$	0.36 ± 0.04	
	$\widetilde{\chi_1} = 0$	0.35 ± 0.02	-		e. 30°	
	Acetone	, 30°	0.335		0.31	
0.193	0.0570	0.29	.369	.1211	.31	
.335		.32	.419			
.399	.1318	.32		$\overline{x}_1 =$	0.30 ± 0.04	
	.1580	.32				
. 532		. 33		llyl chlo		
	$\overline{\mathbf{x}}_1 =$	0.32 ± 0.01			0.31^{a}	
				.0742		
	Propanol		.295	.0953 .1014	.27	
0,138	0.0176	1.12	.310			
.172	.0255	1.00			0.27 ± 0.04	
.206	.0312		Propyl chloride, 40°			
	$\chi_1 =$	1.04 ± 0.06	0.210		0.82	
	Propanol	40°	.299	.0608	.74	
0.960		1.13	.314	.0681	.69	
	.0502			$\tilde{\chi}_1 =$	0.75 ± 0.05	
.348		1.09	т	Propylam	ine 40°	
	.0616				0.61	
$\tilde{\chi}_1 = 1.13 \pm 0.04$.343	.0635 .0825	. 60		
Propanol, 30°		.442		.52		
$0.290 \\ .435$	$0.0248 \\ .0523$	$rac{1}{3}.56^a$		$\overline{\chi}_1 =$	0.59 ± 0.04	
	.0523 .0470	$1.31 \\ 1.41$	Ts	opropyla	mine, 40°	
. 435		1.41 1.29		0.0654		
.507	.0042.0784	1.29 1.20		.0871		
.635	.0890		.488			
		1.30 ± 0.05	. 100		$= 0.66 \pm 0.03$	
a No		l in average.		×1 –	0.00 0.00	
190		i maverage.				

(8) P. J. Flory and W. R. Krigbaum, "Ann. Review of Physical Chemistry," Vol. 2, Annual Reviews, Inc., Stanford, Calif., 1951, p. 383. that due to configurational entropy, when a mole of diluent is added to an infinite amount of polymer at a concentration v_1 .

In column 3 of Table I we have listed values of the parameter χ_1 calculated from the experimental data assuming $p/p_0 = a_1$. It is apparent that χ_1 is not a strong function of concentration for any of the systems studied; in fact with the majority of the diluents χ_1 is constant within the estimated experimental error.⁹ Strictly speaking, eq. 1 is applicable to the data for the swollen polymer only when interactions between polymer segments and diluent molecules are small enough so that random mixing occurs. However, the Flory-Huggins equation clearly affords a reasonable representation of the experimental data, and since values of the interaction parameter χ_1 are small it appears that for the most part polymer-solvent interactions are not large in spite of the polarity of these systems.

large in spite of the polarity of these systems. It can be shown from eq. 1 that for a polymer of infinite molecular weight χ_1 should be greater than 0.5 for limited swelling agents and less than 0.5 for solvents. It may be seen from Table I that with four of the diluents, propanol, propyl chloride, propylamine and isopropylamine, χ_1 is greater than 0.5. Qualitative tests show that propanol is indeed a limited swelling agent; however, the other three of these diluents are completely miscible with polyvinyl acetate. It follows that for the diluents propyl chloride, propylamine and isopropylamine, the χ_1 values must decrease with increasing solvent concentration, ultimately to values below 0.5. Actually for all three of these diluents the limited data of Table I suggest that χ_1 is indeed decreasing with concentration. Factors which might give rise to this concentration dependence have been discussed elsewhere.¹⁰

According to eq. 2, if there is a significant contribution from the enthalpy term, χ_1 should vary linearly with 1/T. We have plotted values of χ_1 against 1/T for the systems acetone-polyvinyl acetate and propanol-polyvinyl acetate. The resulting plots are linear and the $\chi_1 - 1/T$ slopes are, respectively, -290 and 1270. (A plot of χ_1 vs. 1/T has not been made for the benzene-polyvinyl acetate data since for this system the variation of χ_1 with temperature is roughly the same as the estimated experimental error.) By application of the Clausius-Clapeyron equation to these limited χ_1 vs. 1/T data it is possible to obtain an *approximate* estimate of the heats of solution and these may be expressed as

for acetone,
$$\Delta \overline{H}_1 = -0.6 (1 - v_1)^2$$
 kcal. (3a)
for propanol, $\Delta \overline{H}_1 = +2.5 (1 - v_1)^2$ kcal. (3b)

where $\Delta \hat{H}_1$ is the enthalpy change when a mole of diluent is added to an infinite amount of polymer solution at a concentration v_1 . It is notable that $\Delta \hat{H}_1$ is small for the good solvent acetone but larger and positive for the swelling agent, propanol. From the $\Delta \hat{H}_1$ values and eq. 2 it is evident that for both diluents there is a significant entropy contri-

⁽⁹⁾ The estimated experimental errors are different for different systems. Since the largest error is in the pressure reading, the data were least precise for the systems having low values of p_0 .

⁽¹⁰⁾ S. Prager, E. Bagley and F. A. Long, THIS JOURNAL, 75, 2742 (1953).

bution to χ_1 . With the pure polymer and at 40° the entropy for acetone (beyond the configurational) is approximately -2.5 e.u. and for propanol it is approximately 6 e.u. Thus for both systems the data indicate that the entropy contribution to χ_1 is comparable in size to the contribution from the heat of mixing. For both systems the entropy and heat terms give opposing contributions to χ_1 , a result which is in accord with an early discussion by Huggins.¹¹

(11) M. J. Huggins, Ann. N. Y. Acad. Sci., 44, 431 (1943).

DEPARTMENT OF CHEMISTRY

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The Sakaguchi and Biacetyl Reactions for the Identification of Alkyl Guanidines

BY JAMES D. MOLD, JOHN M. LADINO AND E. J. SCHANTZ RECEIVED JUNE 25, 1953

Some representative mono-, di- and trialkyl-substituted guanidines have been prepared and their reactivity to the Sakaguchi¹ and biacetyl² tests has been determined (Table I). Of the compounds tested, only methylguanidine, in which the grouping RNHC (== NH) NH_2 is present, gives a positive Sakaguchi test. Guanidine and the di- and trialkyl substituted compounds do not react even at levels 100-fold as great. These findings are contrary to the report of Poller³ who maintained that the symmetrically substituted di- and trialkyl compounds give positive reactions. Since this worker failed to characterize adequately his test compounds, it is impossible to determine whether these were authentic.

The most intense coloration in the biacetyl reaction for this series of compounds is given by asym-N,N-dimethylguanidine, in which the grouping $RR'NC(=NH)NH_2$ is present. The compounds in which one or both of these alkyl groups are replaced by hydrogen show lower intensities and develop their color at a slower rate. Compounds in which two or three of the nitrogen atoms are substituted with alkyl groups fail to react even at levels 2000-fold as great.

The alkyl guanidines used in this work were prepared by established methods already described in the literature. They were identified by m.p., elementary analysis and alkaline hydrolysis which produced carbon dioxide and volatile amines in the theoretical amounts.⁴ The volatile amines were identified by paper chromatography.⁵ Since these well-characterized compounds were available, potentiometric titrations were carried out to determine their base strengths. All of these compounds were found to have dissociation constants greater than pK_a 11.4 and the titrations did not differ within the experimental accuracy from the values for a water

(1) S. Sakaguchi, J. Biochem. Tokyo, 5, 13, 25 (1925).

(2) A. Harden and D. Norris, J. Physiol., 42, 332 (1911); M. M. Barritt, J. Path. Bact., 42, 441 (1936).

(3) K. Poller, Ber., 59, 1927 (1926); cf. H. Gilman, "Organic Chemistry," Vol. II. 2nd ed., John Wiley and Sons, Inc., New York. N. Y., 1943, p. 1142.

(4) D. D. Van Slyke, J. Biol. Chem., 10, 15 (1911); R. H. A. Plimmer. Biochem. J., 10, 115 (1916).

(5) J. M. Bremner and R. H. Kenten, ibid., 49, 651 (1951).

blank. These results dispute the earlier findings of Davis and Elderfield⁶ that symmetrically substituted dialkyl guanidines are weaker bases than other types of alkyl substituted guanidines. The present work is in agreement with the findings of Neivelt, et al.,7 and of Angyal and Warburton.8

TABLE I

SAKAGUCHI AND BIACETYL REACTIONS OF ALKYL GUANI-

DINES

		-		
Compound		i rea ction ^a Intensity of color ^c	Biacetyl r Amt. tested, µg.	eaction ^b Intensity of color ^d
Guanidine	100	0	6	1.0
Methylguanidine	63 0	1600	5	1.0
asym-N,N-Dimethyl-				
guanidine	362	0	0.5	1.0
sym-N,N'-Dimethyl-				
guanidine	414	0	1000	0
sym-N,N'-Diethyl-				
guanidine	100	0	1000	0
sym-N,N'-Dibutyl-				
guanidine	100	0	1000	0
sym-N,N',N"-Triethyl-	-			
guanidine	100	0	1000	0

^a The procedure used was identical to that described by A. A. Albanese and J. E. Frankston, J. Biol. Chem., 159, 185 (1945), with the exception that 3.5 min. was allowed after the addition of the hypochlorite reagent instead of 1.0 min. as used by these authors. ^b This reaction was carried out according to the directions of P. Eggleton, S. R. Elsden and N. Gough, *Biochem. J.*, 37, 526 (1943). ^o Known concentrations of arginine monohydrochloride (Eastman Kodak Co. Anal.) were used to standardize the procedure. Color intensities were determined with a Coleman colorime-ter using a 530 m μ filter. The intensity is given in terms of μ g. of arginine base. The minimum amount of arginine that could be detected was 1 μ g. ^d Color intensities were determined by comparison with the color produced by known concentrations of creatine hydrate (Eastman Kodak). The intensity is given in terms of μg . of creatine hydrate. The minimum amount of creatine hydrate that could be detected was $0.5 \ \mu g$.

Experimental⁹

Guanidine Hydrochloride (Eastman Kodak Co.).—Anal. Calcd. for CH₆N₈Cl: N, 44.00. Found: N, 44.52, 44.26. Methylguanidine Sulfate.—This compound was pre-pared¹⁰ from dicyanodiamide and methylamine hydrochloride by the procedure of Traube and Gorniak,¹¹ m.p. 238° (lit. m.p. 238°,¹¹ 239–240°,¹² 240°,⁸ 238–239°^{6a}).

Anal. Calcd. for C₄H₁₆N₆SO₄: C, 19.67; H, 6.60. Found: C, 19.64, 19.67; H, 6.55, 6.55.

asym-N,N-Dimethylguanidine Sulfate.—S-Methylisothiourea sulfate was treated with aqueous dimethylamine according to the procedure of Phillips and Clarke,¹² m.p. 278–279° (lit. m.p. 285–288°,¹² 295–297°,⁸ 285–287°6a).

Anal. Calcd. for C₆H₂₀N₆SO₄: C, 26.46; H, 7.40. Found: C, 26.32, 26.47; H, 7.20, 7.35.

(6) (a) T. L. Davis and R. C. Elderfield, THIS JOURNAL, 54, 1499 (1932); (b) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 213-214; H. Gilman, "Organic Chemistry," Vol. II, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1965-1966.

(7) B. Neivelt, E. C. Mayo, J. H. Tiers, D. H. Smith and G. W. Wheland, THIS JOURNAL, 73, 3475 (1951).

(8) S. J. Angyal and W. K. Warburton, J. Chem. Soc., 2492 (1951). (9) Analyses for carbon and hydrogen were by Thomas Shook, for wet carbon by Miss Ann Gerhard; Kjeldahl nitrogen and Sakaguchi determinations by Miss Helen Mathers, and biacetyl determinations by Joseph M. Lynch.

(10) Prepared by Dr. Frank J. Riel.

(11) W. Traube and K. Gorniak, Z. angew. Chem., 42, 379 (1929).

(12) R. Phillips and H. T. Clarke, THIS JOURNAL, 45, 1755 (1923).