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beginning of the second transition around 38350 cm^{-1}, while the 0,0 band of the diffuse bands in α-picoline is taken tentatively as 37640 cm^{-1} and in β-picoline as 37380 cm^{-1}. Again, in γ-picoline the shift goes toward larger wave numbers.

If one assumes that the excitation in pyridine is caused by the π-electrons of the ring as in benzene, then the first two excited electronic levels in pyridine and the picolines are of symmetry types B_1 and A_1 (assuming approximately C_{2v} symmetry for all four compounds). Dr. Gertrud P. Nordheim undertook to calculate roughly the position of the levels on that basis using the MO method. The calculations show that the two levels may be located relatively close in pyridine and that they move closer together in the picolines when a perturbation (of the type described by Wheland and Pauling[3] caused by the substitution of the methyl group is introduced. A close agreement between these theoretical results and the experiments can, of course, not be expected.

Detailed reports on the picoline spectra and their interpretation will be published later.

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Solubility of Heterogeneous Polymers

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SEVERAL years ago, Scott[1] deduced that the critical or consolute point for a solution of a heterogeneous polymer conforming to the Flory[2]–Huggins[3] theory should be determined by the *number-average* molecular weight of the polymer. In view of the very dependence of polymer solubility on molecular weight, this conclusion is highly unexpected; moreover, as pointed out by Spurlin[4] in a recent review, it is not well supported by experiment. In this note the question is reconsidered, and the critical point is found to depend on both *weight-* and *z-average* molecular weights.

For brevity, we start from the equations of Flory[2] (1944) expressing the conditions of equilibrium between a solution (unprimed) and a precipitate (primed):

$$\ln(v_x'/v_x) = \alpha x, \tag{1}$$

$$[2 - (\gamma+1)v_2]\ln[(1-v_2)/(1-\gamma v_2)]$$
$$= 2(\gamma-1)v_2 + \alpha(\gamma+1)v_2 - 2\delta v_2, \tag{2}$$

$$\gamma = \frac{v_2'}{v_2} = \frac{\Sigma v_x'}{\Sigma v_x} = \frac{\Sigma[Q_x^0 e^{\alpha x}/(1+re^{\alpha x})]}{\Sigma[Q_x^0/(1+re^{\alpha x})]}, \tag{3}$$

$$\delta = \frac{\Sigma[Q_x^0(e^{\alpha x}-1)/x(1+re^{\alpha x})]}{\Sigma[Q_x^0/(1+re^{\alpha x})]}, \tag{4}$$

$$\mu = \frac{\alpha + (\gamma-1)v_2 - \delta v_2}{(\gamma-1)v_2[2-(\gamma+1)v_2]}. \tag{5}$$

The notation is that of Flory, in which v_x denotes volume-fraction of x-mer, Q_x^0 the total volume or mass of x-mer (i.e., the molecular weight distribution of the whole polymer), r the ratio of volume of precipitate to volume of solution, and μ the familiar interaction-constant. The physical significance of v_2, α, and γ is clear from Eqs. (1) and (3), while δ is a convenient parameter.

Now, since the two phases must become identical at the critical point, α is zero and γ is unity there. Thus, for states near the critical, the functions of Eqs. (2) to (5) can be expanded as power series in α or $(\gamma-1)$. Accordingly, we first expand the left-hand member of Eq. (2) in powers of $(\gamma-1)$, and develop series in powers of α for the quantities γ and δ of Eqs. (3) and (4). With these latter expressions, γ and δ are then eliminated from the expanded form of Eq. (2). In the

resulting power series in α, the coefficients of α and α^2 vanish identically, while the coefficient of α^3 does not contain the volume-ratio r. Upon letting α approach zero, all higher terms vanish and the critical concentration is found to be

$$(v_2)_c = 1/(1 + x_w x_z^{-\frac{1}{2}}), \tag{6}$$

where

$$x_w = \Sigma x Q_x^0 / \Sigma Q_x^0,$$

and

$$x_z = \Sigma x^2 Q_x^0 / \Sigma x Q_x^0.$$

It is then a simple matter to evaluate the critical value of μ from Eq. (5), the result being

$$2\mu_c = (1 + x_w^{-\frac{1}{2}})^2 + (x_z^{\frac{1}{2}} - x_w^{\frac{1}{2}})^2 / x_w x_z^{\frac{1}{2}}. \tag{7}$$

It is seen that Eqs. (6) and (7) reduce to the previously known results[2] for homogeneous polymers. It should also be noted that the last term of Eq. (7) is negligible for most heterogeneous polymers of interest, so that μ_c (and hence critical temperature or solvent-precipitant ratio) is virtually determined by the weight-average molecular weight.

The method employed above is not a general one for determining a critical state of a multi-component system,[5] but is well suited to the form in which the special relations among the polymeric components (i.e., the molecular weight distribution) are given in the present case. Scott's procedure[1] consisted in equating to zero the first and second derivatives of a_1 (solvent activity) with respect to v_2, and hence failed to take necessary account of the fractionation of the polymer between the two phases; for, while this fractionation vanishes at the critical point, its influence on the derivatives persists. Qualitatively, of course, the solubilizing effect of the smaller polymer molecules on the larger ones, emphasized by Scott, is still seen in the present results, though to a lesser degree.

Applied to equilibria in the two-phase region, the expansions described above soon become unwieldy, except for the case of incipient precipitation ($r=0$). Even here, the equations are scarcely simple for arbitrary molecular weight distributions, and we confine ourselves to the remark that, for $\alpha > 0$, all positive moments of the weight distribution are included. Nowhere does the number-average molecular weight play a role.

There seem to be few published data affording a direct demonstration of these conclusions. An apparent confirmation is found in an experiment of Morey and Tamblyn,[6] who observed that the concentration of non-solvent required to produce incipient precipitation of a mixture of two cellulose acetate-butyrate fractions was equal to that for a single fraction whose molecular weight lies slightly above the z-average of the mixture. However, in this experiment the rate of addition of non-solvent was too rapid to ensure equilibrium. Indeed, in other systems the point of incipient precipitation has been found in this laboratory[7] to depend more nearly on number-average molecular weight, probably because at the high rates of addition of non-solvent employed the precipitation process was diffusion-controlled.

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The Mechanism of the Initiation of the Oxidation of Acetaldehyde in the Gas Phase

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WE recently discovered that small quantities of nitrogen peroxide inhibit the oxidation of acetaldehyde in the gas phase at temperatures between 90 and 140°C. This in-

hibition turns out to be exactly analogous to the inhibition of the polymerization of styrene by quinones,[1-4] and it is similarly found that the length of the induction period is directly proportional to the concentration of the inhibitor. It would thus seem reasonable to assume that this oxidation is also a chain reaction. Under these conditions it is easy to show that the rate of removal of inhibitor, $-dI/dt$, is given by the equation

$$-dI/dt = r_i, \qquad (1)$$

where r_i is the rate of the initiation reaction.

This gives us an experimental criterion for deciding the nature of the initiation step, and we have applied it to investigate the feasibility of our suggested[5] initiation reaction,

$$CH_3CHO + O_2 = CH_3CO + HO_2 \qquad (2)$$

If we assume that most of the inhibitor is consumed during the induction period, τ, then with initiation reaction (2), Eq. (1) becomes

$$I_0/\tau = k_1[CH_3CHO][O_2], \qquad (3)$$

where I_0 is the initial concentration of nitrogen peroxide. Thus a plot of I_0/τ against $[CH_3CHO][O_2]$ should yield a straight line. We have determined I_0/τ for quite a range of concentrations of acetaldehyde and oxygen, and find that Eq. (3) is rigorously obeyed, thus, showing that the initiation is, in fact, a bimolecular reaction between acetaldehyde and oxygen in contrast with the views of earlier work.[6] This does not of course, justify us in completing Eq. (1) in the manner indicated, but a study of the temperature dependence of k_1 leads us to the view that this is the initiation reaction in the temperature range indicated.

A complete account of this work will be published shortly.

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The Isotope Effect in the Decomposition of Oxalic Acid

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A CONSIDERABLE isotope effect in the dissociation of propane 1−C^{13} by electron impact and also in the thermal cracking of C^{13} labeled propane, has been reported by Stevenson et al.[1,2] Their results indicated a 20 percent more frequent rupture of a C^{12}−C^{12} bond than a C^{12}−C^{13} bond in the former case and an 8 percent more frequent rupture in the latter case. Further, Yankwich and Calvin,[3] using C^{14} labeled malonic acid, found an isotope effect in the decarboxylation process, again indicating a preferential splitting of the C^{12}−C^{12} bond over that of the C^{12}−C^{14} bond. We have studied the decomposition of oxalic acid into CO, CO$_2$, and H$_2$O in the presence of concentrated sulphuric acid. In this work, variations in the natural C^{13} content of the oxalic acid and products were measured to determine the isotope effect. This procedure eliminates the need for synthesizing labeled material and reduces certain contamination problems.
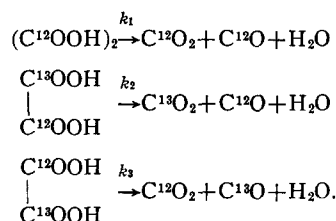
Normal oxalic acid was decomposed in the presence of concentrated sulphuric acid at a controlled temperature. The products of the reaction CO$_2$ and CO were collected and the CO$_2$ separated out in a liquid air trap. The CO was burned to CO$_2$. A third sample of CO$_2$ was prepared by the complete oxidation of a sample of the original oxalic acid. These three samples were then analysed with a mass spectrometer with which their C^{13} contents were compared with a precision of better than 0.1 percent.

TABLE I. C^{13} distribution in oxalic acid decomposition products.

Run	% C^{13}* CO$_2$	% C^{13}* CO	Details	k_2/k_3	$k_1/(k_2+k_3)$
1	1.090		complete	1.040	
		1.059		1.019	
2	1.087		complete	1.034	
		1.050		1.036	
3	1.053		first CO$_2$ evolved		1.034
		1.137	last CO$_2$ evolved		

* Percent C^{13} in oxalic acid—1.069, temperature of runs—100°C.

Two effects have been observed: (1) a preference for the C^{13} to appear in the CO$_2$ rather than the CO; (2) a higher rate of decomposition of oxalic acid molecules containing only C^{12} carbon atoms over those containing C^{13} atoms. These two effects can be expressed quantitatively in terms of the three specific rate constants defined by the equations:

$$(C^{12}OOH)_2 \xrightarrow{k_1} C^{12}O_2 + C^{12}O + H_2O$$

$$\begin{matrix} C^{13}OOH \\ | \\ C^{12}OOH \end{matrix} \xrightarrow{k_2} C^{13}O_2 + C^{12}O + H_2O$$

$$\begin{matrix} C^{12}OOH \\ | \\ C^{13}OOH \end{matrix} \xrightarrow{k_3} C^{12}O_2 + C^{13}O + H_2O.$$

If these are first-order reactions, then

$$\frac{(C^{12}O_2)}{(C^{13}O_2)} = \frac{(C^{13}O)}{(C^{12}O)}$$

$$= \frac{Ox^{12}(1-e^{-k_1 t}) + Ox^{13}(1-e^{-(k_2+k_3)t})\dfrac{k_3}{k_2+k_3}}{Ox^{13}(1-e^{-(k_2+k_3)t})\dfrac{k_2}{k_2+k_3}}. \qquad (1)$$

If reaction is carried to completion ($t = \infty$), then

$$\frac{(C^{12}O_2)}{(C^{13}O_2)} = \frac{(C^{13}O)}{(C^{12}O)} = \frac{Ox^{12}(k_2+k_3) + k_3 Ox^{13}}{k_2 Ox^{13}}, \qquad (2)$$

where Ox^{12} and Ox^{13} are the number of moles of the two isotopic species of oxalic acid in starting material.

As seen from Eq. (2), the ratio k_2/k_3 can be calculated from either the C^{13} abundance data for the CO$_2$ or the CO. The results of Table I give $k_2/k_3 = 1.033$. If there were no isotope effects in (1), k_2/k_3 would equal unity.

If, instead of carrying out the reaction to completion, a very small fraction of the oxalic acid is decomposed, so that the C^{13} content of the oxalic acid can be assumed to remain constant, then Eq. (2) becomes

$$\frac{(C^{12}O_2)}{(C^{13}O_2)} = \frac{(C^{13}O)}{(C^{12}O)} = \frac{k_1 Ox^{12} + k_3 Ox^{13}}{k_2 Ox^{13}}. \qquad (3)$$

Thus, from a C^{13} analysis of the first CO$_2$ or CO to be evolved from a 3-gram sample of oxalic acid, the ratio $k_1/(k_2+k_3)$ can be determined. The difference between this ratio and unity is a measure of the second isotope effect mentioned above. The ratio $k_1/(k_2+k_3)$ turns out to be 1.034.

Again it is seen that the isotope effects in unidirectional processes are appreciable, amounting in this case to 3.5 percent. The fact that C^{13} is favored in the CO$_2$ seems to indicate a preferential splitting of the C^{12}−O^{16} bond over that of the C^{13}−O^{16} bond, although it seems likely that the C−C bond is also involved because of the second isotope effect. Further experiments are in progress to determine also the distribution of O^{18} between the products of the reaction.

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