The continuous line shows the value of $-\dfrac{dM}{dt}\cdot(\eta)$ for benzoyl peroxide over a wide range of concentrations. This has been included as it shows that with 'good' catalysts and fairly high catalyst concentrations the activity is independent of changes of catalyst concentration. This point is important since all peroxides decompose at different rates ; hence the comparison has been made at equal rates of polymerization. The fall in the curve at lower concentrations is probably due to the more noticeable effect of transfer reactions. (As at this stage the results are purely comparative, it is not considered necessary to use the power relationship which has been established between (η) and the molecular weight ; the constancy of the product of the reaction-rate and intrinsic viscosity over a wide range is fortuitous.)

The activity, according to this point of view, is shown by the values of the ordinates for the various catalysts relative to the standard catalyst, benzoyl peroxide. The position on the abscissa is of less importance, though in some cases it gives an indication of the rate of decomposition of the catalyst. The results shown, which are mainly obtained from substituted benzoyl peroxides, support the view that electron-attracting substituents give radicals of low activity, particularly when this is supplemented by the mesomeric effect. On the other hand, electron-repelling groups increase the activity of the radical.

In the case of alkoxy benzoyl peroxides, the mesomeric effect outweighs and reverses the inductive effect, consequently the activity of the radical is high. (This result is supported by U.S.P. 2,419,347, claiming high catalytic activity for o-alkoxy benzoyl peroxides.) However, di(3-4-methylene dioxybenzoyl) peroxide has a low activity, suggesting that the observed effect is purely inductive. Halogens have similar activities with the same orientation : the two results shown for di-p- and -m-chlorobenzoyl peroxides are in the expected positions. (Many of the results are in a similar order to those found for the dissociation constants of the substituted benzoic acids. In addition, an 'ortho' effect is shown by all ortho-substituted benzoyl peroxides.) Alkyl groups, as would be expected, increase the activity ; but there is little difference between the effects of different alkyl groups. A result for an aliphatic acyl peroxide is given, and, as would be expected, this shows high activity. The introduction of a double bond (dicrotonyl peroxide) increases the rate of reaction, possibly by an increase in the rate of decomposition, and causes a slight fall in activity. Replacement of the methyl in this peroxide by phenyl, however, in dicinnamoyl peroxide, stabilizes the radical, which is consequently of lower activity.

These results seem to indicate that an important characteristic of a free radical is the availability of the free electron for reaction with the π-electrons of the double bond.

This work forms a part of a larger investigation which will be given in detail elsewhere.

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[1] J. Amer. Chem. Soc., 64, 1621 (1942).
[2] Mayo, F. R., Lewis, F. M., and Walling, C., "Labile Molecule", Faraday Society Discussion (September 1947).

Transformation of Frequency Distributions

FREQUENCY distributions of numbers of eggs, insects, spores, or other biological entities are descriptive of discrete variation, and can never be represented *exactly* by a normal distribution or by any other distribution of a continuous variate. Nevertheless, when the number of observations and the range of variation is large, such distributions may often be *adequately* represented by a continuous distribution. Experience has shown that transformation of discrete counts to a scale of $\sqrt{n}$, log n, or log $(n + 1)$ may considerably assist the representation by a normal distribution.

The device of plotting the cumulative distribution in probit units against a proposed square root or logarithmic scale of counts, as suggested by Gaddum[1], is useful as a rapid test of whether or not the right normalizing transformation has been found : if the distribution is effectively normal on the transformed scale, the probits will be linearly related to the counts. Spiller[2] has recently commented on this procedure. He has stated that statistical analysis in terms of this linear regression seems preferable to argument from the parent distribution, but that methods of calculating regressions and variance do not appear to be available.

In all uses of probit methods, however, the parent distribution must be kept in mind. The standard methods of calculation associated with probit analysis[3] have been devised for data in which the cumulative distribution is estimated directly from the observations, and they are clearly not appropriate here. The regression equation for a diagram such as that drawn by Spiller is, in fact, a line which attains a probit value of 5·0 at the mean value of the sample (on the transformed scale), and which has a slope equal to the reciprocal of the standard deviation of the sample ; an application of statistical theory to the problem of estimating this line would show that the parameters of the line were to be obtained from that mean and standard deviation. As Gaddum has stated, "The best estimates of the mean and standard deviation will be obtained by applying the ordinary methods directly to the transformed observations".

Some idea of the values of the parameters may be formed by measurement of the diagram. For example, Spiller's line B has a value of about 0·70 for log $(n + 1)$ at a probit of 5·0, and an increase of unity in log $(n + 1)$ corresponds to a probit increase of about 1·9. Hence the distribution of log $(n + 1)$ may be regarded as approximately normal, with mean 0·70 and standard deviation 0·53 ($= 1/1·9$) ; these compare with values, calculated from Spiller's table, of 0·774 for the mean and 0·487 for the standard deviation. The size of the standard deviation relative to the mean suggests that agreement with a normal distribution cannot be very close (though it may be good enough for comparisons between samples to be made with the aid of normal distribution theory), and comparison of the frequency polygon with the calculated distribution would confirm this. The probit diagram may indeed be deceptive for data of this kind, since considerable deviations from normality are not always apparent by inspection of it.

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[1] Gaddum, J. H., Nature, 156, 463 (1945).
[2] Spiller, D., Nature, 162, 530 (1948).
[3] Finney, D. J., "Probit Analysis" (London : Camb. Univ. Press, 1947).