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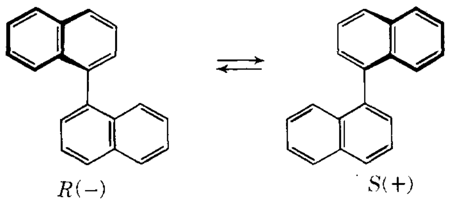
Carbon Catalyzed Racemization of 1,1′-Binaphthyl

Sir:

The industrially important carbon blacks and activated carbons are widely used as supports for metal catalysts and, by themselves, are known to catalyze numerous inorganic reactions.[1] However, catalytic reactivity with organic substrates is reported only for some oxidation-reduction reactions[2,3] and for a few polymerizations and cationic isomerizations.[4,5] We report here the high activity of carbon in promoting racemization of optically active 1,1′-binaphthyl.[6] The known[7,8] uncatalyzed reaction in solution is a simple nonpolar transformation which involves only rotation around the single bond joining the two naphthalene rings.



Decolorizing carbons rapidly racemize solutions of binaphthyl in acetone within a few minutes. For example, 0.015 *M* binaphthyl is 93% racemized in 10 min at room temperature in the presence of 1.7 mg/ml of Norit SG1. In contrast, the uncatalyzed rate of racemization corresponds to a half-life of 12 hr at 20°. To compare the activity of various carbons the reaction was studied simply by stirring the catalyst at 20° with binaphthyl in acetone. The racemization was quenched by filtering out the catalyst, and solutions were analyzed using normal polarimetric means. The activity of an individual batch of catalyst, with different operators and apparatus and with different rates of stirring, was consistent among various runs although different batches of the same commercial carbon gave different rates.[9] Some results, treated as first-order reactions, are shown in Figure 1.

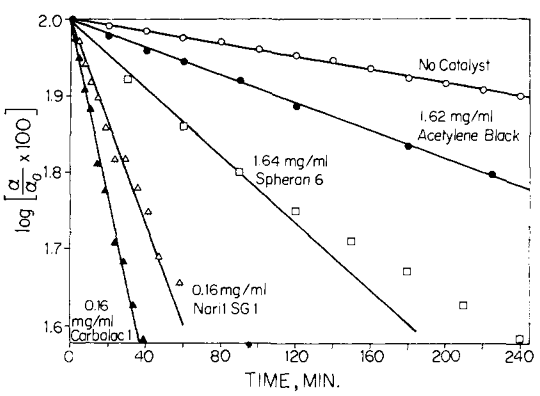


Figure 1. First-order plots for racemization of 0.015 *M* 1,1′-binaphthyl in acetone at 20° in the presence of various carbon catalysts.

The observed activity (Sterling FT0 < acetylene black < Spheron 6 < Norit < Carbolac 1) parallels the surface/weight ratios of these carbons (15.7, 64, 110, *ca.* 750, and 1000 m^2/g, respectively).[10] Graphitized Spheron 6 (2700°) was less active than Spheron 6 itself, while graphite (grade SP-1) has no observable catalytic properties. Spheron 6, which is a well-characterized carbon black,[10,11] was chosen for more detailed kinetic studies. Kinetic plots showed some deviation from first-order behavior which is apparent after about one half-life (see curve for Spheron 6 in Figure 1). Control experiments showed this was not due to any progressive deactivation of catalyst by standing with binaphthyl in acetone. In any case, initial first-order rate constants were calculated, and representative data are presented in Table I.

The observed first-order rate constants at 20° are proportional to catalyst concentration (at 0.015 *M* binaphthyl), decrease with increasing binaphthyl concentration (at 1.6 mg/ml catalyst concentration), and are extraordinarily sensitive to small concentrations of compounds with structures similar to binaphthyl. At 0.015 *M* binaphthyl with 1.6 mg/ml of Spheron 6 only 10^{-5} *M* perylene is sufficient to poison the catalyst. On the other hand, although use of benzene as a solvent prevents catalytic activity, dilute (10^{-3} *M*) solutions of benzene in acetone have no effect on catalytic activity. Compounds with a greater number of fused aromatic rings are increasingly effective inhibitors (benzene < naphthylene < anthracene < pyrene < perylene). Competitive adsorption by these compounds is no doubt the cause of the inhibition effects. In this regard it should be noted that binaphthyl itself is not noticeably adsorbed (*i.e.*, 0 ± 2% by uv and glc analysis) by Spheron 6 under the conditions of the kinetic runs.

The kinetic results are well correlated by the following

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[1] The literature on active carbon is immense. Some recent monographs are (a) J. S. Mattson and H. B. Mark, Jr., "Activated Carbon," Marcel Dekker, New York, N. Y., 1971; (b) M. Smíšek and S. Černy, "Active Carbon," Elsevier, Amsterdam, 1970; (c) see also V. R. Deitz, "Bibliography of Solid Adsorbents," National Bureau of Standards, Washington, D. C., 1944; (d) *Nat. Bur. Stand.* (*U. S.*), *Circ.*, 566 (1956).

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[4] (a) L. W. Hill V. K. Acharya, and W. E. Wallace, Jr., *Carbon* (*Oxford*), **9**, 219 (1971); (b) P. H. Given and L. W. Hill, *ibid.*, 6, 525 (1968).

[5] T. W. J. Taylor and E. M. W. Lavington, *J. Chem. Soc.*, 980 (1934).

[6] R. E. Pincock and K. R. Wilson, *J. Amer. Chem. Soc.*, **93**, 1291 (1971).

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[8] A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, **68**, 651 (1964).

[9] A sample of Spheron 6 from year 1957 was more than twice as active as Spheron 6 supplied in 1970.

[10] Surface areas are determined by nitrogen adsorption; see (a) C. L. Mantell, "Carbon and Graphite Handbook," Interscience, New York, N. Y., 1968, pp 98–103; (b) W. R. Smith and D. C. Bean in "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed, Vol. 4, Interscience, New York, N. Y., 1964, pp 243–282; private communication from American Norit Co., Inc., Jacksonville, Fla.

[11] P. H. Given and L. W. Hill, *Carbon* (*Oxford*), 7, 649 (1969).

Table I. Initial First-Order Rate Constants at 20° for Spheron 6 Catalyzed Racemization of 1,1′-Binaphthyl in Acetone

Binaphthyl concn, *M*	Catalyst concn, mg/ml	I concn, $M \times 10^4$	$k_{\text{obsd}} \times 10^5$, sec^{-1}
0.015	0	0	1.64
0.015	0.78	0	4.65
0.0149	1.56	0	8.41
0.0151	3.11	0	16.6
0.030	1.61	0	4.08
0.0065	1.62	0	22.7
0.0037	1.62	0	29.6
0.015	1.58	0.92[a]	5.91
0.015	1.58	1.37[a]	5.72
0.015	1.57	1.87[a]	5.44
0.015	1.57	3.78[a]	4.63
0.015	1.57	7.57[a]	3.39
0.0149	1.55	7.79[b]	1.93
0.0149	1.58	70.8[c]	7.73

[a] Naphthalene. [b] Anthracene. [c] Benzene.

reaction scheme where R and S stand for enantiomeric forms of binaphthyl, C* denotes active sites on the carbon catalyst, C*B is the catalyst–binaphthyl complex, I is an inhibitor, and C*I is the inactivated inhibitor–catalyst complex.

$$\mathrm{R} \overset{k_{\text{unc}}}{\rightleftharpoons} \mathrm{S}$$

$$\mathrm{R} + \mathrm{C^*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C^*B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{S} + \mathrm{C^*}$$

$$\mathrm{C^*} + \mathrm{I} \underset{k_{-\mathrm{I}}}{\overset{k_{\mathrm{I}}}{\rightleftharpoons}} \mathrm{C^*I}$$

With the assumption of equal reactivities of R and S enantiomers (*i.e.*, $k_1 = k_{-2}$ and $k_2 = k_{-1}$) the following relationship for the observed first-order rate constants may be obtained. This type of equation for heterogeneous catalysis[12] is similar to the familiar kinetic equation for enzyme kinetics with competitive inhibition and strengthens the suggested analogy of carbon catalyzed reactions (*e.g.*, hydrogen peroxide decomposition by carbon blacks)[13] with enzymatic reactions.[3,14] Small increases in rates of racemization of binaphthyl brought about by high concentrations of complexing agents have been studied by Colter;[15] the catalysis by carbon is much more effective, with activities for a high surface carbon such as Carbolac 1 comparable with that of some enzymatic reactions.[16] The general correlation of rates with surface areas, the inhibition or poisoning by planar polyaromatic compounds, and the planar nature of the transition state for noncatalyzed racemization of binaphthyl would all seem to indicate that the active sites of these catalysts are the surface planes of the graphite-like crystallites of carbon. A flattened binaphthyl molecule on the planar surface of activated carbon is an attractive model for the transition state for catalyzed racemization. However, the possibility of reaction at more specific sites, possibly on the active edge positions of the planes, can not definitely be ruled out.

$$k_{\text{obsd}} = 2k_{\text{unc}} + \frac{2k_1k_2[\mathrm{C}_{\text{total}}]}{k_1[\text{binaphthyl}] + 2k_2 + 2k_2k_{\mathrm{I}}[\mathrm{I}]/k_{-\mathrm{I}}}$$

Acknowledgment. This work was supported by grants from the National Research Council of Canada. We thank Professor Gilbert Hooley for samples of various carbons and for helpful suggestions.

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(16) With 0.015 *M* binaphthyl and 1.6 mg/ml of Carbolac 1 the conversion rate at 20° is 2.6×10^{-6} mol min^{-1} mg^{-1}. From the average diameter of a particle of catalyst (122 Å) and with a density of 1.86 g/cm^3, the average turnover number may be estimated at *ca.* 2.8×10^3 (mol of binaphthyl) (min)$^{-1}$ (mol of carbon particles)$^{-1}$. Enzymatic turnover numbers are in the range 1–10^6 (mol of substrate) (min)$^{-1}$ (mol of enzyme)$^{-1}$. The activity of a single site on carbon may be much less than that of an active site on an enzyme; however, with carbon, low individual activity is probably made up for by the presence of a great many sites on a particle.

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Photoelectron Spectra of 2,3-Diazabicyclo[2.2.*n*]alk-2-enes (*n* = 1, 2, 3, 4)

Sir:

An interesting application of photoelectron spectroscopy (pes) is the study of the interaction between nitrogen "lone pairs." Pes has been used to establish the splitting of the n_+ and n_- orbitals in *trans*-azomethane,[1] diazirine,[2] and substituted diazirines[2,3] and to examine the relative importance of through-space *vs.* through-bond interactions[4] between the "lone pairs" in 1,4-diazabicyclo[2.2.2]octane.[5] Furthermore, a recent pes study of some tetralkylhydrazines[6] indicates that the splitting of "lone pair" orbitals may, at least in some cases, reflect certain structural differences or similarities between the members of a class of related molecules.

In this communication we report a pes study of a series of cis azo molecules, namely the first four 2,3-diazabicyclo[2.2.*n*]alk-2-enes.[7]

It is evident that the pe spectra (Figure 1) of these molecules are characterized by a relatively broad band for the first IP and a somewhat sharper onset for the second band which appears to overlap with one or more

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(1) E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **8**, 878 (1969); E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970).

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(6) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973).

(7) The compounds 1(*n*) were prepared and purified as described elsewhere.[8] The pe spectra were recorded on a previously described spectrometer[9] and calibrated with xenon; conventional sample handling was used for 1(1–3) while, owing to its low volatility, 1(4) required a direct inlet to the collision chamber and was heated to 30°.

(8) M. L. Heyman, V. T. Bandurco, and J. P. Snyder, *Chem. Commun.*, 297 (1971).

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