A repeat run at 195° for 12 hr. used up all the starting material and gave tar but no identifiable product.

Reaction of 1,3-Dibromo-2,2-dimethylpropane with Sodium Iodide.—A mixture of the dibromide (55 g., 0.24 mole), sodium iodide (105 g., 0.71 mole) and dimethylformamide was heated at 120° for 5 hr. The contents of the Dry Ice–acetone traps, 6.95 g., was twice fractionated through a 40-plate concentric tube column yielding: fraction A, b.p. 21°, 1.65 g.; fraction B, b.p. 38–39°, 4.1 g.; 1.2 g. of intermediate fractions. The gas phase infrared spectrum (200 mm.) of A was identical to that of an authentic sample of 1,1-dimethylcyclopropane.[28] The spectrum of B (200 mm.) was identical to that of authentic 2-methyl-2-butene. From the original reaction mixture there was recovered, after dilution with water and extraction with ether, 7.1 g. (13% recovery) of starting dibromide.

When 1,1-dimethylcyclopropane (1 ml.) was heated in a sealed tube with sodium iodide (0.5 g.), iodine (0.5 g.) and dimethylformamide (3 ml.) at 150° for an hour, 90% of pure starting material was recovered. No trace of 2-methyl-2-butene was found.

When 1,3-dibromo-2,2-dimethylpropane (5 g.) was heated with iodine (1 g.) in dimethylformamide (10 ml.) at 155° for 15 hr., there was obtained only a 92% recovery of material identical in all respects to the starting material.

Reaction of 1,3-Dibromo-2-methylpropane with Sodium Iodide.—A mixture of dibromide (8 g., 0.037 mole), sodium iodide (15 g., 0.1 mole) and acetamide (50 g.) was heated at 160° for 6 hr. The contents of the Dry Ice–acetone traps was distilled bulb to bulb four times, yielding 1.1 g. (53%) of colorless volatile liquid. Its gas phase infrared spectrum (200 mm.) was identical to that of an authentic sample of 2-methylpropene. From the original reaction flask there was recovered 0.5 g. (6% recovery) of starting dibromide.

When methylcyclopropane (1 ml.) was heated with sodium iodide (1 g.) and iodine (1 g.) in acetamide (3 g.) in a sealed tube at 150–175° for an hour, there was obtained a 75% recovery of volatile material that had the infrared spectrum of pure methylcyclopropane.

When 1,3-dibromo-2-methylpropane (1 g.) was heated with iodine (0.2 g.) and acetamide (3 g.) at 160° for 6 hr., the only product obtained, 0.65 g., was identical in all respects with starting dibromide.

Reaction of 1,3-Dibromopropane with Sodium Iodide.—A mixture of 1,3-dibromopropane (Eastman Kodak Co., redistilled, 40.4 g., 0.2 mole), sodium iodide (60 g., 0.4 mole) and dimethylformamide (200 ml.) was heated at 170° for 5 hr. while a slow stream of dry nitrogen was passed through. The contents of the Dry Ice–acetone traps were distilled bulb to bulb three times giving 3.6 g. of volatile hydrocarbon whose infrared spectrum (gas, 200 mm.) was identical to that of an authentic sample of propylene. From the reaction flask there was recovered 7.1 g. of starting dibromide and 3.1 g. of what was probably 1,3-diiodopropane, b.p. 219–222° (lit.[29] b.p. 224°). The latter contained iodine but not bromine, failed to react with sodium iodide and gave silver iodide when allowed to stand with alcoholic silver nitrate.

When 1,3-dibromopropane (20 g.) was heated with iodine (4 g.) and dimethylformamide (50 ml.) at 170° for 6 hr., no volatile material was formed, and 1,3-dibromopropane was recovered in 90% yield. At room temperature, the dibromide slowly precipitated sodium bromide when treated with sodium iodide in acetone. With alcoholic silver nitrate, the dibromide slowly precipitated silver bromide.

Treatment of 1,3-Dibromo-2-phenylpropane with Sodium Iodide.—A mixture of dibromide (5 g., 0.018 mole), sodium iodide (6 g., 0.04 mole) and acetamide (20 g.) was heated at 190° for 6 hr. A carbon tetrachloride extract of a portion of the darkened reaction mixture was colorless, indicating the absence of iodine. The reaction mixture was diluted with water (100 ml.) and the resultant tarry mixture was extracted with ether. Evaporation of the dried ether extract left no residue. The insoluble tar was subjected to steam distillation, but no water-insoluble distillate was obtained.

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[28] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. W. Boord, THIS JOURNAL, **70**, 946 (1948).

[29] J. Timmermans and T. J. F. Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA]

The "Element Effect" as a Criterion of Mechanism in Activated Aromatic Nucleophilic Substitution Reactions[1,2]

BY J. F. BUNNETT, EDGAR W. GARBISCH, JR., AND KENNETH M. PRUITT

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Rates of condensation of nine 1-substituted-2,4-dinitrobenzenes with piperidine in methanol to form 2,4-dinitrophenylpiperidine (II) have been measured. Three substituents, fluorine, nitro and *p*-toluenesulfonoxy, are displaced very rapidly while six substituents are displaced more slowly with remarkably little variation in rate amongst the six. Since displacement of these six substituents involves the breaking of bonds between carbon and five other elements, this result indicates that bond-breaking has not made significant progress in the rate-determining transition states of these reactions. The strictly SN2-like mechanism is thereby eliminated, but an alternate one-step mechanism is not. However, the facts are most agreeably interpreted in terms of the intermediate complex mechanism with the step in which the complex I is formed being rate determining. This result has the same significance for these nucleophilic substitutions that Melander's observation of the lack of a hydrogen isotope effect in nitration and bromination had for those reactions. Interesting complications were encountered in several of the reactions studied, but these did not prevent satisfactory determination of the desired rate coefficients.

The mechanism of activated[3] aromatic nucleophilic substitution reactions has become a subject of some controversy in recent years. The principal contending points of view are, on the one hand, that the mechanism is a direct, one-step displacement much like the aliphatic SN2 mechanism (equation 1), and on the other hand that the reaction occurs in two steps and involves an intermediate of some stability (equation 2). Both points of view have been advocated at various times through the years, but the strongest arguments have been presented recently by Chapman and his associates,[4] for the one-step, SN2-like mech-

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[1] Research supported by the Office of Ordnance Research, U. S. Army.

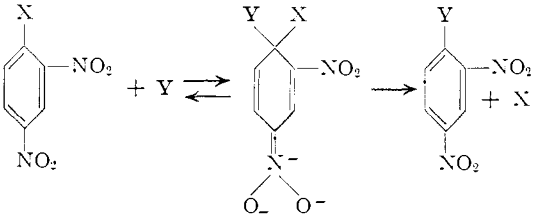
[2] Presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1956; preliminary results were described at the Southeastern Regional A.C.S. Meeting, Birmingham, Ala., October, 1954.

[3] It has seemed desirable to distinguish, in discussions of mechanisms, aromatic nucleophilic substitution reactions activated by nitro or other strongly electron-attracting groups from those occurring without activation, as in unsubstituted phenyl or naphthyl halides.

[4] (a) N. B. Chapman and R. E. Parker, *J. Chem. Soc.*, 3301 (1951); (b) E. A. S. Cavell and N. B. Chapman, *ibid.*, 3392 (1953); (c) N. B. Chapman, R. E. Parker and P. W. Soanes, *ibid.*, 2109 (1954).

anism, and by Bunnett and Zahler[5] for the two-step mechanism involving a metastable intermediate.

$$\text{Ar–X} + \text{Y} \longrightarrow \text{Ar–Y} + \text{X} \qquad (1)$$



(2)

I

The situation is somewhat like that which prevailed in the field of electrophilic aromatic substitution in 1948, at which time both one-step and two-step mechanisms were seriously advocated for reactions such as nitration but no really decisive experiments had been published. A major advance in the field of electrophilic substitution was Melander's[6] demonstration that there is no hydrogen isotope effect in typical nitration and bromination reactions, that is, that tritium and protium are displaced at essentially identical rates. This showed that breaking of the carbon–hydrogen bond had made little or no progress in the rate-determining transition states of these reactions. Melander's result was sometimes taken as disproof of the one-step mechanism, but Hammond[7] pointed out that it was not incompatible with a one-step mechanism in which C–H bond breaking had not made significant progress in the transition state. However, recent kinetics studies[8,9] coupled with isotope effect measurements have established the two-step, intermediate complex mechanism for certain diazo coupling and deformylation reactions and this mechanism now seems extremely probable for all bimolecular electrophilic aromatic substitutions.

The "Element Effect."—Isotope effect experiments similar to Melander's would be desirable in the field of nucleophilic aromatic substitution but unfortunately cannot be done so conveniently. Hydrogen itself is not commonly replaced, and when it is the reaction is probably more complicated than a mere one- or two-step displacement. In theory the isotope effect in replacement of, for example, a nitro group or a chlorine atom (that is, the ratio of rates of displacement of ^{14}N *vs.* ^{15}N or of ^{35}Cl *vs.* ^{37}Cl) could be used as a criterion of mechanism, but the effect would at greatest be small and measurements would have to be made with great exactitude before they could have significance.

On the other hand, it is possible to study the "element effect" in nucleophilic substitutions, that is, the change in rate as the first atom of the displaceable group X is changed from one element to another. It is well known that the rates of cleavage of C–Z bonds are strongly dependent on the identity of the element Z.[10] The differences in rates are much greater than the differences in the rates of cleavage of C–H bonds as the hydrogen atom is changed from one isotope to another. Therefore, if C–X bond breaking has made significant progress in the transition state of the rate-determining step, the rates of displacement of groups whose first atoms represent diverse elements should differ greatly from one another.

If breaking of the C–X bond has not made significant progress in the rate-determining transition state, that is, if the activation process is entirely or almost entirely concerned with attachment of the nucleophilic reagent Y to the aromatic substrate, the effect of changing the first atom of the displaceable group is less easily predicted. Because various groups, differing in their first atoms and in other ways, have different electronic and steric characteristics, it is to be expected that changes in the group X will have some effect on the rate of attachment of the nucleophilic reagent Y to the aromatic substrate. Yet, if the groups are of moderate size and of similar inductive effect their effects on the rate of the attachment process may not differ very much.

Thus it is expected that there will be *great* differences in the rates of displacement of groups whose first atoms represent diverse elements if the C–X bond is partially or wholly ruptured in a rate-determining process. On the other hand, if the C–X bond remains intact during the activation process, the differences in rate may be small though it is not excluded that groups with exceptional steric or electronic effects on the bond-formation process may be displaced at exceptional rates. Therefore, the only result from a study of the "element effect" that would have meaning as a criterion of mechanism would be a sameness of rate as the first atom was changed from one element to another.

It is, however, necessary to reckon with the possibility that two groups with first atoms representing different elements might, if partial C–X bond breaking does occur in the activation process, be displaced at similar rates owing to coincidence of compensating factors. On this account, similarity of rates of displacement of more than two such groups would have to be observed before the effect could be considered as proof that bond-breaking was not involved in the activation process. The chance that similarity of rates could arise from mere coincidence would drop rapidly to the vanishing point as the number of groups displaced at similar rates increased. It must be emphasized, though, that if several groups with different first atoms were displaced at similar rates, indicating that bond-breaking was not part of a rate-determining process, it would still be possible for other groups to be displaced much faster or much slower without the conclusion being invalidated insofar as the groups displaced at similar rates were concerned.

Having examined the potentialities and the limitations of the "element effect" as a criterion of mechanism, let us now turn to an experimental study of the "element effect" in a typical activated aromatic substitution process. The displacement of 1-substituents from 1-substituted-2,4-dinitro-

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(5) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 297 (1951).

(6) L. Melander, *Arkiv Kemi*, **2**, 213 (1950).

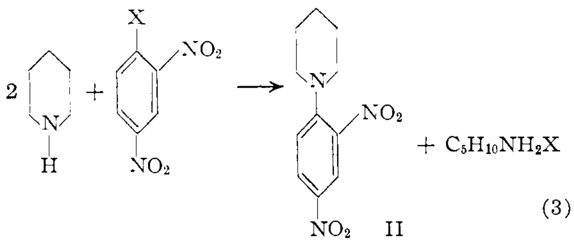
(7) G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(8) H. Zollinger, *Helv. Chim. Acta*, **38**, 1597 (1955).

(9) W. M. Schubert and H. Burkett, THIS JOURNAL, **78**, 64 (1956); W. M. Schubert and P. C. Myhre, private communication.

(10) K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1183 (1937).

benzenes by piperidine (equation 3) was chosen for study. Many reactions in this series occur at convenient rates in methanol, and the rates are easily determined by photometric measurements. Some complications were encountered in the kinetics study, and these are discussed later in this paper, but in all cases excepting one it was possible to determine precise rate coefficients for displacement of the 1-substituents by piperidine.



II

(3)

Kinetics Results.—Second-order rate coefficients for the series of reactions represented by equation 3 are listed in Table I. Also, energies and entropies of activation are given for all reactions studied at more than one temperature. The data show[11] that three substituents, the fluorine atom and the nitro and *p*-toluenesulfonoxy groups, are replaced with great rapidity, while all the rest are replaced at nearly the same rate. The maximum variation in rate among the last six substituents in Table I is fivefold, and excepting the iodine atom the maximum variation among the remaining five is only 56%.

TABLE I

REACTIONS OF 1-SUBSTITUTED-2,4-DINITROBENZENES WITH PIPERIDINE

1-Substituent	Rate coefficient, 0.0°, l. mole^{-1} min.$^{-1}$	Relative rate	ΔE, kcal./mole	$\Delta S^{\ddagger}$, cal./deg.
F	90	3300		
NO_2	24.2	890		
$OSO_2C_6H_4CH_3$-*p*	2.72	100		
SOC_6H_5	0.129[a]	4.7	10.8[a]	−33.3[a]
Br	.118	4.3	11.8	−29.5
Cl	.117	4.3	11.6	−30.2
$SO_2C_6H_5$	.0860	3.2	12.0	−29.3
$OC_6H_4NO_2$-*p*	.0812	3.0	10.5[a]	−35.3[a]
I	.0272	1.0	12.0	−31.7

[a] From runs in presence of piperidine hydrochloride.

These six groups have first atoms representing five elements. As discussed above, the possibility that such similarity of rates could arise by coincidence, if bond-breaking were part of the activation process, is vanishingly small. Thus this situation meets the stringent requirements that must be met if a firm conclusion is to be drawn from a study of the "element effect." The conclusion is that breaking of the C–X bond has not made significant progress in the rate-determining transition states of these displacements.

This conclusion is reinforced by the similarity of the energies and entropies of activation for the six reactions. This indicates that the similarity in rates is deep-seated, and is a further indication that the phenomenon is no mere coincidence.

Now, we may ask, to what extent does this result settle the question as to whether the reaction has a one-step, SN2-like or a two-step, intermediate complex mechanism? This much can be said: The results are thoroughly compatible with the intermediate complex mechanism with the first (bond formation) step rate-determining. The results are thoroughly incompatible with a mechanism strictly like that of SN2 displacements at saturated carbon atoms, or with any other mechanism in which any bond formation to Y requires partial breaking of the C–X bond. The reason is that in the "transition state" of any such mechanism if the C–X bond is essentially intact the C–Y bond must be essentially nil, and it is then not possible to account for the substantial activation energies of these reactions. However, there is a one-step mechanism having a superficial resemblance to that of SN2 displacements which cannot be rigorously excluded on the basis of the present data.

This alternate mechanism is best discussed with reference to an energy profile for the reaction (Fig. 1). The solid line is for a reaction occurring by the intermediate complex mechanism with the first step rate-determining. Point III represents the transition state III for formation of the intermediate and point IV represents the transition state IV for its decomposition to form products. The alternate one-step mechanism has the same energy profile except that the broken line is followed between points III and IV. Both mechanisms involve the same rate-determining transi-

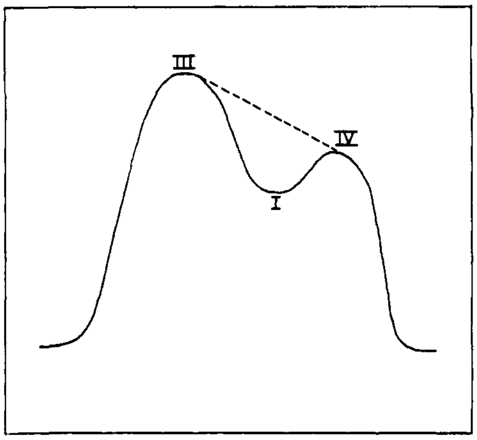
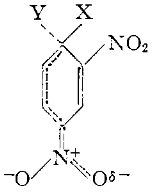
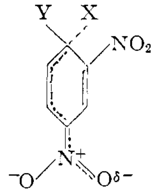


Fig. 1.—Energy profiles: solid line, for the intermediate complex mechanism; broken line for an alternate, one-step mechanism.



III



IV

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[11] The approximate positions of the four halogens and the nitro and *p*-nitrophenoxy groups in this reactivity series might have been inferred from results of various workers with other aromatic nucleophilic substitution reaction series; *cf.* reference 5, p. 332.

tion state III with the C–X bond fully intact and the C–Y bond partially formed. It does not seem profitable to attempt to assign exact physical significance to the broken line in Fig. 1, although it might be thought to represent a concerted completion of the C–Y bond and partial rupture of the C–X bond in such a way that there is little change in the total bond order of the C–X plus C–Y bonds during the change from state III to IV. This alternate one-step mechanism is regarded as most unlikely for several reasons based on considerations of analogy. Also, it requires an unusual strict division of action between various phases of a one-step mechanism.

Summarizing briefly, the present experiments are in agreement with the intermediate complex mechanism but eliminate the strictly SN2-like mechanism. They can also be interpreted in terms of an alternative one-step mechanism which is disfavored on other grounds, though not disproved.

The conclusion drawn from the present work is, strictly speaking, applicable only to those six reactions which occurred at similar rates, but it can be inferred to apply to other nucleophilic substitutions showing similar characteristics such as similar ratios of halogen mobility. Thus it is inferred that in the displacement of halogens from activated aryl halides by other amines,[4c,5] by alkoxides[12] and by thiophenoxide ion,[13] the carbon–halogen bond is not significantly ruptured in the rate-determining transition states.

Consideration of the replaceability of fluorine also leads to a similar conclusion. In many common aromatic nucleophilic displacements, including the reactions cited in the previous paragraph as well as the reaction series studied in the present work, fluorine is displaced faster than the other halogens by as much as several thousand-fold. In other processes, especially aliphatic SN1 and SN2 reactions[10,14] and the formation of benzyne from aryl halides,[15] fluorine is much less easily removed than are the other halogens. Heterolytic breaking of the carbon–fluorine bond is characteristically slower, under comparable conditions, than heterolysis of any other carbon–halogen bond. It follows that C–F bond-breaking cannot have made significant progress in the transition state of any substitution in which fluorine is the most rapidly replaced of the halogens.

That aryl fluorides are often so reactive means, then, that attachment of a nucleophilic reagent to an unsaturated carbon atom is particularly accelerated by a fluorine substituent on that carbon. Miller, Fainberg and Fried[16] have reached the same conclusion from experiments of a quite different type. They found that in the SN2′ reactions of halide ions with fluoroallyl halides, γ-fluorine substituents accelerate the reaction although they are not replaced. For example, $Cl^- + CF_2{=}CFCF_2I \rightarrow CClF_2CF{=}CF_2 + I^-$. The γ-fluorine substituents aid the attachment of the nucleophilic reagent to the γ-carbon atom but, because heterolysis of carbon–fluorine bonds is comparatively slow, some other halogen is expelled as a halide ion.

Recently, fluorine has been found to be the least rapidly replaced of the halogens in reactions of activated aryl halides with N-methylaniline[17] or with iodide ion.[18] It is recognized that this resemblance to the order of halogen mobility in aliphatic SN2 reactions indicates that bond-breaking is involved in a rate-determining process. Hammond and Parks[17] pointed out that the result with N-methylaniline is intelligible in terms either of the intermediate complex mechanism with the second step contributing to rate-determination or of a one-step mechanism with the old (C–F) bond considerably ruptured in the transition state. Fierens and Halleux,[18b] on the other hand, interpreted the result with iodide ion only in terms of a one-step displacement. We should like to comment that their result, like that of Hammond and Parks, is also intelligible in terms of the intermediate complex mechanism.

Complications in the Kinetics Study.—Of the nine reactions summarized in Table I, only those in which the four halogens were displaced occurred quantitatively in methanol as represented by equation 3. The other five furnished less than quantitative yields of II under the same conditions, as shown in Table II. It was suspected that methoxide ion, generated by interaction of piperidine with the solvent might be a competing nucleophilic reagent.[19] If so, addition of piperidinium ions to the medium ought to repress the ionization and obliterate the competition. In three cases (Table II), in which the groups displaced were nitro, phenylsulfonyl and *p*-nitrophenoxy, the yield rose to 100% when the reaction was run in the presence of piperidine hydrochloride. Thus methoxide ion is shown to be responsible for the competing reactions in the absence of added piperidinium ion.

With 2,4-dinitrodiphenyl sulfone, the competing reaction is probably displacement of the 4-nitro group; Leandri and Tundo[20] have reported that the reaction of this sulfone with methoxide ion produces 4-methoxy-2-nitrodiphenyl sulfone. With 1,2,4-trinitrobenzene and 2,4,4′ trinitrodiphenyl ether, the competing reaction is undoubtedly displacement of the 1-substituents by methoxide ion.[21]

The fact that the methanolysis complication ap-

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[12] (a) C. W. L. Bevan, *J. Chem. Soc.*, 2340 (1951); (b) A. L. Beckwith, J. Miller and G. D. Leahy, *ibid.*, 3552 (1952); (c) G. P. Briner, J. Miller, M. Liveris and P. G. Lutz, *ibid.*, 1265 (1954); (d) B. A. Bolto, J. Miller and V. A. Williams, *ibid.*, 2926 (1955).

[13] J. F. Bunnett and W. D. Merritt, Jr., unpublished work.

[14] N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1673 (1952); C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 246 (1953).

[15] J. D. Roberts, D. A. Semenow, H. E. Simmons and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

[16] W. T. Miller, A. H. Fainberg and J. Fried, "Congress Handbook, XIVth International Congress of Pure and Applied Chemistry," Zürich, Switzerland, July, 1955, p. 55.

[17] G. S. Hammond and L. R. Parks, THIS JOURNAL, **77**, 340 (1955).

[18] (a) J. Cortier, P. J. C. Fierens, M. Gilon and A. Halleux, *Bull. soc. chim. Belg.*, **64**, 709 (1955); (b) P. J. C. Fierens and A. Halleux, *ibid.*, **64**, 717 (1955).

[19] Competition of this sort has been noted before; *cf.* reference 5, p. 344; reference 4b; also J. F. Bunnett and R. J. Morath, THIS JOURNAL, **77**, 5051 (1955).

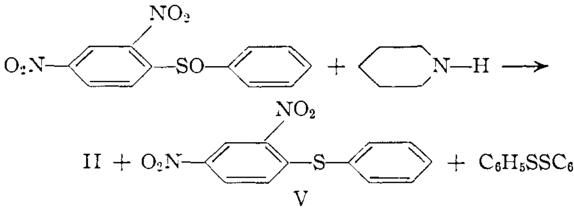
[20] G. Leandri and A. Tundo, *Ann. Chim. (Rome)*, **44**, 479 (1954).

[21] A. F. Holleman and F. E. van Haeften, *Rec. trav. chim.*, **40**, 97 (1921); Y. Ogata and M. Okano, THIS JOURNAL, **71**, 3211 (1949).

peared in some reactions and not in others indicates a dependence of the comparative nucleophilic reactivity of the two reagents on the substrate attacked.[22] Specifically, the nucleophilic reactivity of methoxide ion, relative to piperidine as a standard, is less for the displacement of halogen atoms from 1-halo-2,4-dinitrobenzenes than it is for the displacement of certain other groups from other substrates. Nearly twenty years ago, Loudon and his co-workers[23] observed similar effects in reactions of several nucleophilic reagents with various chloronitrodiphenyl sulfones.

The yield of II from 2,4-dinitrophenyl *p*-toluenesulfonate was only 55% and it was not significantly higher in the presence of piperidine hydrochloride. The competing reaction in this case was shown[24] to be displacement at the sulfur atom producing *p*-toluenesulfonpiperidide. Here the competition is between two electrophilic centers in the same substrate for the one nucleophilic reagent, piperidine.

The reaction with 2,4-dinitrodiphenyl sulfoxide was by far the most complicated. Some of the products have been isolated, and they include 2,4-dinitrodiphenyl *sulfide* (V) and diphenyl disulfide as well as II. Photometric examination of the product mixture, with assumption that II and V are the only colored products formed, indicated that these two products were formed (at 0°) to the extent of 25 and 26%, respectively, in the absence of piperidine hydrochloride, and to the extent of 73 and 16% when piperidine hydrochloride was present. The assumption is possibly wrong, but even if correct a considerable fraction of the dinitrophenyl groups is left unaccounted for. The fact that the yield of II was greatly increased by addition of piperidine hydrochloride suggests that methoxide ion competes strongly with piperidine for the sulfoxide. On the other hand the fact that the yield of V is relatively insensitive to the presence of piperidine hydrochloride indicates that methoxide ion is not uniquely responsible for the generation of this product.[25]



In spite of the complexity of the reaction with the sulfoxide, it displays decent pseudo-first order kinetics (*cf.* Fig. 2). There is some uncertainty as to just what fraction of the total rate of destruction of the sulfoxide should be assigned to the production of II, but the uncertainty is defined within limits and the rate coefficients reported are probably not in error by more than 20%.

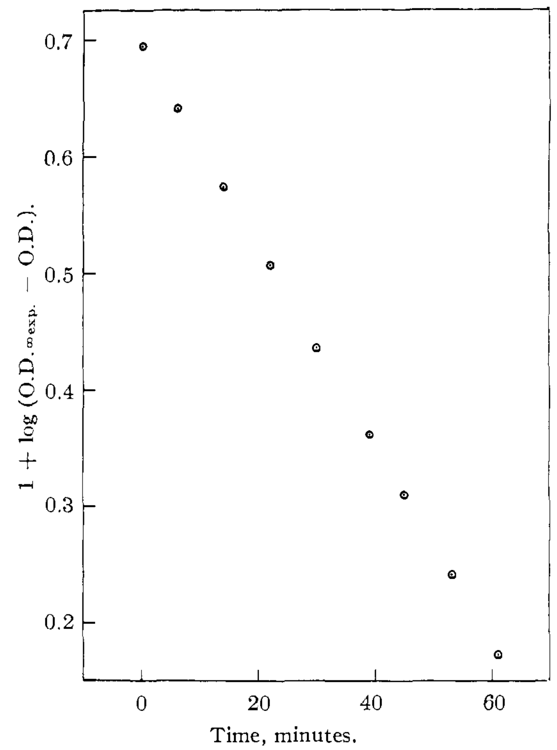


Fig. 2.—Plot of data from a reaction of 2,4-dinitrodiphenyl sulfoxide with piperidine in methanol at 0.0° (piperidine hydrochloride absent). The total first-order rate coefficient from this run is 1.97×10^{-2} min.$^{-1}$, and the rate coefficient for the reaction forming II is 5.01×10^{-3} min.$^{-1}$. The second-order rate coefficient for the reaction forming II is 0.122 l. mole^{-1} min.$^{-1}$.

Experimental

Piperidine was purified by refluxing over sodium for six hours and then distilling from sodium. Reagent grade methanol was dried by the method of Hartley and Raikes.[26] **Piperidine hydrochloride** was formed by combining piperidine and hydrogen chloride in ether; after recrystallization from absolute ethanol, it melted at 244–245° (lit.[27] 245°).

2,4-Dinitrodiphenyl Sulfoxide.—To a hot solution of 8.22 g. (0.030 mole) of 2,4-dinitrodiphenyl sulfide in 50 cc. of acetic acid, a solution of 3.38 g. of 30% hydrogen peroxide solution (containing 0.030 mole hydrogen peroxide) in 15 cc. of acetic acid was added. The mixture was heated 2.5 hours on the steam-bath, and the product was precipitated by pouring the reaction mixture into water. After preliminary crystallizations from methanol, which did not effect much purification, the product was crystallized twice from carbon tetrachloride. 2,4-Dinitrodiphenyl sulfoxide was obtained as dense clumps of yellow crystals, m.p. 114.5–115.5°.

Anal. Calcd. for $C_{12}H_8N_2O_5S$: C, 49.31; H, 2.76. Found: C, 48.97; H, 2.83.

Several early preparations had melting points near 115°, and then one preparation carried out in the standard manner furnished a product of m.p. 127.5–129°. Thereafter all preparations melted about 129°, and the lower melting material on being recrystallized from methanol was transformed into the higher melting form.

2,4-Dinitroiodobenzene,[28] **1,2,4-trinitrobenzene**[29] and **2,4-**

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[22] Such dependence has been noted in several instances recently in this Laboratory.

[23] J. D. Loudon and N. Shulman, *J. Chem. Soc.*, 722 (1941), and earlier papers.

[24] Unpublished work in this Laboratory by Mr. J. Y. Bassett, Jr.

[25] The sulfide V is not, as we now see it, formed by direct reduction of the sulfoxide. Rather, we think that benzenesulfenate ions, produced during the original cleavage of the sulfoxide by piperidine or methoxide, may undergo transformations resulting in the production of thiophenoxide ions which then attack the sulfoxide to form V plus more benzenesulfenate ions. The matter is under investigation by Messrs. R. F. Snipes and B. F. Hrutfiord.

[26] H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

[27] D. Vorländer and T. Wallis, *Ann.*, **345**, 286 (1906).

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dinitrodiphenyl sulfone[30] were prepared by standard procedures. **2,4-Dinitrofluorobenzene, 2,4-dinitrochlorobenzene** and **2,4-dinitrobromobenzene** were commercial products repurified.

2,4-Dinitrophenyl *p*-toluenesulfonate was prepared from sodium 2,4-dinitrophenoxide and *p*-toluenesulfonyl chloride in acetone medium. After recrystallization from methanol, it melted at 122° (lit.[31] 124°). **2,4,4′-Trinitrodiphenyl ether** was prepared by condensation of 2,4-dinitrochlorobenzene with potassium *p*-nitrophenoxide in aqueous dioxane medium. After crystallization from ethanol and then from 1:1 chloroform:carbon tetrachloride (with charcoal), it melted at 115–116.5° (lit.[32] 116°).

Kinetics Measurements.—Standard solutions of piperidine, of piperidine hydrochloride and of the various substrates in methanol were prepared. Each run was commenced by pipetting a standard volume of substrate solution into a volumetric flask. A standard volume of piperidine hydrochloride solution was next added in some runs. Then much of the necessary methanol was added and the flask was placed in the thermostat. When thermal equilibrium had been attained, a standard volume of the piperidine solution (at thermostat temperature) was added by pipet and immediately the flask was filled to the mark with thermostated methanol. The flask was quickly removed, shaken thoroughly, and replaced in the thermostat. A sample of the reacting solution was removed by fast-delivery pipet and discharged at once into a 50-cc. volumetric flask about half full of "quenching solution" (0.05 *N* sulfuric acid in 50% ethanol). The time of release into the quenching solution was recorded, and other samples were similarly removed and quenched at recorded times. For runs at 0°, the pipet was kept in an ice-cooled chamber when not being used for sampling. Samples were withdrawn during a period of from one to six half-lives. The reaction flask was left in the thermostat for a period of at least eight half-lives, and then an "experimental infinity" sample was removed and quenched in the usual way. A "mock infinity" solution, containing 2,4-dinitrophenylpiperidine (II) in methanol in the concentration expected on the assumption of a quantitative yield, was prepared and a sample of it was also quenched in the standard manner. All the volumetric flasks containing quenched samples were filled to the mark with quenching solution and shaken thoroughly. The optical densities of the resulting solutions were determined in a Beckman model B spectrophotometer at 380 mμ.

The concentration of piperidine in all runs was about 0.04 *M*. Piperidine hydrochloride, when used, was 0.02 *M* in the reaction solutions. The substrate was about 0.001 *M*.

For runs with 2,4-dinitrofluorobenzene, the procedure was modified in detail but not in principle so as to allow faster work with the reaction. Erlenmeyer flasks were used both for reaction solutions and for quenching solutions; their wide mouths facilitate fast manipulations. With two men working together, it was possible to prepare the reaction solution and remove four samples by pipet within 45 seconds. The resulting plots were linear, but the agreement between runs was not as good as for other reactions.

Comparison of the "experimental" and "mock" infinity optical densities indicated what yield of II had been obtained, except in the reactions of 2,4-dinitrodiphenyl sulfoxide as discussed below. The logarithm of (experimental infinity optical density less optical density of any sample) was plotted against the appropriate time for each sample in a run; in nearly every case the resulting plot was a straight line similar to Fig. 2. The slope of the line, usually obvious from visual inspection but determined by the method of least squares if there was any scatter, multiplied by 2.303 gave the total first-order rate coefficient for destruction of the substrate. This multiplied by the yield (the ratio of "experimental" to "mock" infinity optical densities) gave the first-order rate coefficient for the reaction forming 2,4-dinitrophenylpiperidine.[33] This was then divided by the initial piperidine concentration to get the second-order rate coefficient for the reaction with piperidine. Results are listed in Table II. In one case, comparison with a directly measured second-order coefficient is possible: for the reaction of 2,4-dinitrochlorobenzene with piperidine in methanol at 30.06°, we found *via* the pseudo first-order coefficient k_2 = 0.965 whereas Bunnett and Morath[34] measured directly 0.935 l. mole^{-1} min.$^{-1}$.

TABLE II

REACTIONS OF 1-SUBSTITUTED-2,4-DINITROBENZENES WITH PIPERIDINE IN METHANOL

1-Substituent	Temp., °C.	Added substance	Yield of II, %	Mean rate coefficient,[a] l. mole^{-1} min.$^{-1}$
F	0.0	....	100	89.8[b]
NO_2	.0	....	98	[c]
	.0	$C_5H_{10}NH_2Cl$	100	24.2[d]
$OSO_2C_6H_4CH_2$-*p*	.0	....	55	2.72[d]
	.0	$C_5H_{10}NH_2Cl$	58	2.65
SOC_6H_5	.0	....	25	0.122
	.0	$C_5H_{10}NH_2Cl$	73	.129
	25.22	....	28	.655[d]
	25.22	$C_5H_{10}NH_2Cl$	74	.718[d]
	46.00	....	29	1.92[d]
	46.00	$C_5H_{10}NH_2Cl$	74	2.36[d]
Br	0.0	....	100	0.118[d]
	30.06	....	100	1.014[d]
Cl	0.0	....	100	0.117[d]
	30.06	....	100	.965[d]
$SO_2C_6H_5$	0.0	....	92	.0860[d]
	0.0	$C_5H_{10}NH_2Cl$	100	.0898
	25.22	....	92	.558[d]
	25.22	$C_5H_{10}NH_2Cl$	100	.574
$OC_6H_4NO_2$-*p*	0.0	....	98	.0812[e]
	7.68	....	97	.128
	14.89	....	96	.204
	0.0	$C_5H_{10}NH_2Cl$	100	.0794
	25.48	$C_5H_{10}NH_2Cl$	100	.416[d]
	45.97	$C_5H_{10}NH_2Cl$	100	1.30[d]
I	0.0	....	100	0.0272
	7.67	....	100	.0488
	14.92	....	100	.0855

[a] Second-order rate coefficients for the reactions forming 2,4-dinitrophenylpiperidine are listed. [b] Average of four runs; average deviation: 5.9%. [c] In this run, a precise rate coefficient was not obtained. [d] Average of two runs; average deviation: 1% or less. [e] Average of two runs; average deviation: 4.2%.

The Arrhenius activation energy, ΔE, and the entropy of activation, $\Delta S\ddagger$, were calculated from standard expressions.[35]

Reaction Products.—The absorption spectra of "experimental infinity" solutions from reactions with 1,2,4-trinitrobenzene, 2,4,4′-trinitrodiphenyl ether, 2,4-dinitrodiphenyl sulfone and 2,4-dinitrophenyl *p*-toluenesulfonate closely resembled that of a "mock infinity" solution; this is evidence that the expected II had actually been formed. II was isolated from reactions with 2,4-dinitrophenyl *p*-toluenesulfonate[24] and from 2,4-dinitrodiphenyl sulfoxide (below).

The Reaction of 2,4-Dinitrodiphenyl Sulfoxide with Piperidine.—To a solution of 0.88 g. (0.003 mole) of 2,4-dinitrodiphenyl sulfoxide and 2.43 g. (0.02 mole) of piperidine hydrochloride in 900 cc. of reagent grade methanol, a solution of 3.42 g. of purified piperidine in 100 cc. of methanol was added with swirling. The temperature after mixing was 21°. The solution was allowed to stand overnight and then was evaporated nearly to dryness on the steam-bath at reduced pressure.

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[30] R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

[31] K. Freudenberg and H. Hess, *Ann.*, **448**, 129 (1926).

[32] L. C. Raiford and J. C. Colbert, THIS JOURNAL, **48**, 2660 (1926).

[33] This treatment involves the reasonable assumption that the competing reactions occur in constant ratio throughout a run; *cf.* A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953 p. 148.

[34] J. F. Bunnett and R. J. Morath, THIS JOURNAL, **77**, 5165 (1955).

[35] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Process," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

Some benzene was added and evaporation was continued until separation of solids made further evaporation difficult. A mixture of 35 cc. of concentrated hydrochloric acid and 5 cc. of water was added. The solids dissolved and the two layers were separated. Addition of sodium carbonate to the aqueous layer caused the separation of an orange solid which was taken up in benzene. The residue from evaporation of the benzene was crystallized from absolute ethanol. Orange crystals, m.p. 92–94° not depressed on admixture with authentic II, weighing 0.35 g. were obtained; a second crop weighing 0.08 g. melted at 90–92.5°. The total yield of II was 57%.

The benzene layer from the first separation was evaporated nearly to dryness and chromatographed on alumina. The material eluted rapidly by petroleum ether was crystallized from 95% ethanol. 2,4-Dinitrodiphenyl sulfide (V) (0.13 g., 16%) was obtained as yellow crystals, m.p. 116.5–120° not depressed on admixture with an authentic sample. A second crop of light yellow crystals, weight 0.06 g., was recognized as diphenyl disulfide by its melting point, 55–60° not depressed on admixture with an authentic sample. No other well-defined substances were obtained from the chromatographic column.

From a reaction similar but for the absence of piperidine hydrochloride, a 38% yield of II and an approximately 6% yield of V were isolated. (The formation of V was first observed in preliminary experiments by Mr. R. F. Snipes.)

The yields of II and V under the conditions of the kinetics runs were estimated by a photometric procedure. Since V absorbs appreciably at 380 $m\mu$, the optical density of the usual "experimental infinity" sample from 2,4-dinitrodiphenyl sulfoxide is not a valid measure of the yield of II. The modified procedure depends on the facts that II is colorless at 380 $m\mu$ in a "super quenching solution" (equal volumes of water, 95% ethanol and concentrated sulfuric acid) whereas V actually absorbs somewhat more strongly in "super quenching solution." Samples from typical runs allowed to go to completion were therefore quenched both in the usual way and in "super quenching solution." It was assumed that the optical density of the "super-quenched" solution was due wholly to V; from this value and from the known ratio of the optical densities of V in the usual and the "super" quenching solutions, it was possible to calculate what part of the optical density of the sample quenched in the usual way was due to V. The optical density due to II was then obtained by subtraction. Yields estimated in this manner were as follows: at 0°, 25% II and 26% V; at 0° in presence of piperidine hydrochloride, 73% II and 16% V; at 25.2°, 28% II and 18% V; at 25.2° in presence of piperidine hydrochloride, 74% II and 15% V; at 46.0°, 29% II and 14% V; at 46.0° in presence of piperidine hydrochloride, 74% II and 15% V. These estimates, being based on an assumption of uncertain validity, are only approximate, but reassurance is gained from the fact that rate coefficients for the formation of II in the absence and in the presence of piperidine hydrochloride calculated from the yields so estimated, are in fair agreement (Table II).

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Steric Inhibition of Hyperconjugation[1,2]

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The various manners are examined in which steric strain between an alkyl radical R linked to a bulky radical R' can be relieved. It is concluded that torsional rotation can inhibit hyperconjugative resonance of cyclopropyl, but not of methyl or *t*-butyl groups, and can reduce, but not inhibit completely, hyperconjugative resonance of ethyl and isopropyl radicals. Of the other possible modes of reduction of steric strain, out of plane bending of the alkyl group appears the most effective means of inhibiting hyperconjugative resonance. Stretching of the bond between R and R', and compression of the radical R are considered rather ineffective in inhibiting hyperconjugation. None of the modes considered are believed to be able to inhibit *completely* hyperconjugative resonance except for cyclopropyl groups, nor is any of them considered to be very effective in inhibition.

It has been suggested recently that hyperconjugative resonance may be inhibited sterically[3] in a manner resembling the well established steric inhibition of resonance[4] of radicals such as the nitro and substituted amino groups. A theoretical examination of the possibilities of steric inhibition of hyperconjugative resonance of alkyl groups seems indicated, particularly in the light of a recent theoretical investigation of hyperconjugation of the relatively complex ethyl and *t*-butyl groups.[5] Since the various alkyl radicals have different steric requirements, the various basic radicals, methyl, ethyl, isopropyl, *t*-butyl and cyclopropyl will be discussed separately. Before proceeding to discuss each group, we shall examine the various ways in which steric strain can be relieved. Assume an alkyl radical R attached to another radical R′ of sufficient complexity to produce a steric strain between R and R′. The possible ways in which R can be deformed from its "normal" configuration then include the following: (1) rotation (torsional) about the R–R′ bond; (2) stretching of the R–R′ bond; (3) bending of the R–R′ bond; (4) compression of the bond angles within the radical R; (5) further stretchings or distortions within the group R. The last of these is unlikely to be important, and will not be discussed further. Of all these modes, only torsional rotation involves no reduction in σ-bond energy, and hence is the deformation most likely to be involved in the reduction of steric strain. Information concerning the resistance to deformation of the remaining modes is available from a knowledge of force constants. Since torsional rotation of the rather bulky alkyl groups, however, cannot be very effective in relieving steric strain, some of the other modes must also be considered. It must then be realized that involvement of these deformations may cause changes in the σ-bonds and their energies and possibly in hybridization, and that the resulting effects on reactivity and spectra might be difficult to separate

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[2] Paper V in the series "Molecular Orbital Theory of Valence." For paper IV see *Z. Elektrochem.*, **59**, 823 (1955).

[3] *E.g.*, Illuminati, *Gazz. chim. ital.*, **83**, 905 (1953).

[4] *Cf.* G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 136 ff., 160 ff., 185 ff., 272 ff.

[5] Y. I'Haya, *Bull. Chem. Soc. Japan*, **28**, 369 (1955).