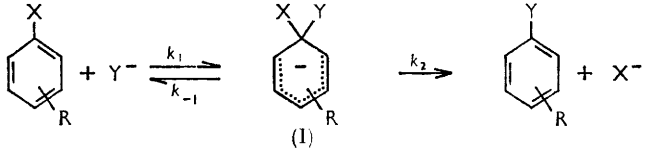
994. *The Properties of Meisenheimer Addition Complexes.*

By L. K. Dyall.

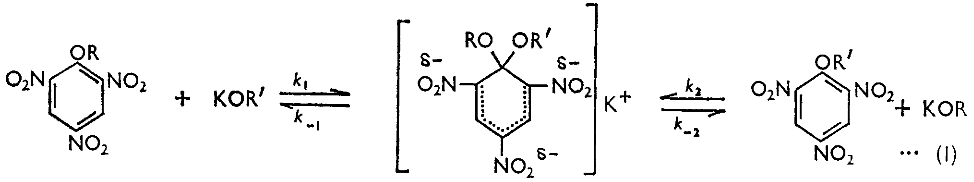
The infrared spectra of seven Meisenheimer addition complexes are reported and interpreted in terms of a fully covalent structure. The significance of these complexes in activated aromatic nucleophilic substitution is discussed. It is confirmed that the compositions of the mixtures of products obtained on treating Meisenheimer addition complexes with acid are determined by the relative anionic stabilities of the displaced groups.

The most widely accepted mechanism of aromatic nucleophilic substitution can be represented as follows:[1-4]



(I)

The observed mobility orders for displacement of halogen from activated aromatic substrates, some of which suggested[5,6,7] a mechanism analogous to S_N2 displacement at saturated carbon atoms, can be accounted for by assuming suitable relative magnitudes of k_1, k_{-1}, and k_2.[2,8,9] Bunnett and Zahler[1] favour a fully covalent structure for the intermediate (I), with sp^3-hybridization at the seat of substitution; the transition state is assumed to approximate closely to this structure. Some support for this mechanism was adduced by Brower:[10] experiments at high pressures showed that the transition states for activated nucleophilic substitution of bromonaphthalenes and bromoquinolines[11] with methoxide ion or piperidine closely resemble the structure (I), and for both nucleophiles the transition states have similar locations on the reaction co-ordinate. Other evidence for the intermediate-complex mechanism has been summarized by Bunnett.[2] The mechanism has however been criticized. Fierens and Halleux,[12] and Chapman and his co-workers[5,13] state that the transition state is not a constant, completely localized structure, but rather that it involves a change in hybridization at the attacked carbon atom *towards* sp^3, the degree of hybridization depending on both the nucleophile and the



(II) ··· (1)

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[1] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[2] Bunnett, *Quart. Rev.*, 1958, **12**, 1.
[3] Berliner, Quinn, and Monack, *J. Amer. Chem. Soc.*, 1950, **72**, 5305.
[4] Berliner and Monack, *J. Amer. Chem. Soc.*, 1952, **74**, 1574.
[5] Chapman and Russell-Hill, *J.*, 1956, 1563.
[6] Fierens *et al.*, *Bull. Soc. chim. belges*, 1955, **64**, 696, 704, 709, 717.
[7] Hammond and Parks, *J. Amer. Chem. Soc.*, 1955, **77**, 340.
[8] Bunnett and Randall, *J. Amer. Chem. Soc.*, 1958, **80**, 6020.
[9] Bunnett, Garbisch, and Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385.
[10] Brower, *J. Amer. Chem. Soc.*, 1959, **81**, 3504.
[11] Brower, *J. Amer. Chem. Soc.*, 1958, **80**, 2105.
[12] Fierens and Halleux, *Bull. Soc. chim. belges*, 1955, **64**, 717.
[13] Chapman and Rees, *J.*, 1954, 1190.

substrate. A similar criticism was raised by Hammond, Parks, and Hawthorne,[14] who showed that the transfer of charge from benzoate ions to the substrate (1-chloro-2,4-dinitrobenzene) has made very little progress in the transition state. Other workers think that expression (I) is one extreme of an intermediate with a hybrid structure.[15,16]

These criticisms concern the proximity of the transition-state structure to that of the intermediate (I), and do not necessarily question the structure of the intermediate. The present paper concerns the structure of the intermediate. The intermediate-complex mechanism depends for much of its plausibility on the isolation of intermediates from the reactions of alkoxides with picryl ethers. The Meisenheimer addition complex (II) can be prepared by either of the routes shown.

The identity of samples of the product (II) prepared by the two different reaction paths has been proved by the equivalence of the ultraviolet spectra[17] and of the infrared spectra[18] and by the composition of the mixtures of picryl ethers produced on treatment of the complex with acid.[19,20,21] This has generally been accepted as proof that compound (II) has a fully covalent structure, but the proof is not unequivocal. The complex (II) may be of the charge-transfer type, and reaction (1) could then be written as follows:

$$\mathrm{PicOR} + \bar{\mathrm{O}}\mathrm{R}' \rightleftharpoons \underset{\mathrm{(III)}}{(\mathrm{PicOR},\bar{\mathrm{O}}\mathrm{R}')} \rightleftharpoons \underset{\mathrm{(IV)}}{(\mathrm{PicOR}',\bar{\mathrm{O}}\mathrm{R})} \rightleftharpoons \bar{\mathrm{O}}\mathrm{R} + \mathrm{PicOR}'$$

If one of the charge-transfer complexes (III) and (IV) is appreciably more stable than the other, then only one complex would be isolated. The rôle of charge-transfer complexes in aromatic nucleophilic substitution is not yet known. Although charge-transfer complex formation has been reported[22,23,24] in reaction mixtures involving nucleophilic substitution, it is not clear whether the steps of complex formation and substitution are competing or successive.

The present paper reports the infrared spectra of seven Meisenheimer addition complexes and interprets them in terms of possible structures. The compositions of the mixtures of picryl ethers produced by treatment of the complexes with dilute sulphuric acid are determined and discussed in terms of ease of anion loss from the intermediate (II).

EXPERIMENTAL

M. p.s are corrected. Analyses are by the C.S.I.R.O. and University of Melbourne Microanalytical Laboratory.

Purification of Alcohols.—Methanol was distilled from phosphoric acid, and the distillate was dried by refluxing it with iodine and magnesium turnings. The anhydrous alcohol was then fractionated (b. p. 65·1°/764 mm.) from 2,4,6-trinitrobenzoic acid; it had n_D^{20} 1·3281. Ethanol was purified by treatment with freshly ignited quicklime, followed by further drying with iodine and magnesium turnings and distillation; it had n_D^{20} 1·3615. Benzyl alcohol was shaken with solid potassium hydroxide and then distilled at reduced pressure; the distillate was heated for 6 hr. with quicklime on a water-bath, filtered, and redistilled (b. p. 45°/0·4 mm.; n_D^{20} 1·5397). Propan-2-ol was shaken with sodium hydroxide,[25] distilled from anhydrous potassium carbonate, and fractionated, then having b. p. 82·5°/762 mm., n_D^{20} 1·3773.

Preparation of Picryl Ethers.—Phenyl picryl ether was prepared in 77% yield by treating

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[14] Hammond, Parks, and Hawthorne, *J. Amer. Chem. Soc.*, 1955, **77**, 2903.
[15] Chapman and Parker, *J.*, 1951, 3301.
[16] Bevan, *J.*, 1951, 2340.
[17] Foster, *Nature*, 1955, **176**, 746.
[18] Foster and Hammick, *J.*, 1954, 2153.
[19] Meisenheimer, *Annalen*, 1902, **323**, 205.
[20] Farmer, *J.*, 1959, 3425.
[21] Earle and Jackson, *Amer. Chem. J.*, 1903, **29**, 89.
[22] Kuntz and Ross, *J. Amer. Chem. Soc.*, 1954, **76**, 3000.
[23] Ainscough and Caldin, *J.*, 1956, 2528.
[24] Kosower, *J. Amer. Chem. Soc.*, 1956, **78**, 3497.
[25] Gilson, *J. Amer. Chem. Soc.*, 1932, **54**, 1445.

picryl chloride (12·2 mmoles) in methanol (20 ml.) dropwise (10 min.) with sodium phenoxide (12·2 mmoles) in methanol (10 ml.) at 0°. After 30 min. at room temperature, the mixture was diluted with water and the solid product was collected. Phenyl picryl ether crystallized from benzene–light petroleum as very pale yellow prisms, m. p. 156·0—156·5° (lit., 153°) (Found: C, 47·0; H, 2·5; N, 13·7. Calc. for $C_{12}H_7N_3O_7$: C, 47·2; H, 2·3; N, 13·7%). Benzyl, ethyl, and methyl picryl ether were prepared by treatment of picryl chloride with the appropriate sodium alkoxide, in solution in the corresponding alcohol, and each ether was crystallized from its parent alcohol to constant m. p. and analytical purity. An attempted preparation of isopropyl picryl ether by this method led to tars, and 17% of the picryl chloride was recovered; substitution of acetone for the propan-2-ol used as solvent similarly resulted in reduction, and no starting material was recovered. Isopropyl picryl ether (m. p. 94—95°; lit., 95°) was prepared in 45% yield from isopropyl iodide and silver picrate[26] (Found: C, 40·1; H, 3·6; N, 15·3. Calc. for $C_9H_9N_3O_7$: C, 39·9; H, 3·35; N, 15·5%).

Preparation of Addition Compounds.—The general method is described for the preparation of potassium methyl 1-ethoxypicrate. A solution of potassium ethoxide (0·79 mmole in 10 ml. of ethanol) was added dropwise during 10 min., with shaking, to methyl picryl ether (0·82 mmole) in ethanol (10 ml.) at 0°. The apparatus and solutions were protected by quicklime drying-tubes. After 15 min. at 0°, the mixture was diluted with dry benzene (20 ml.) to assist precipitation of the red crystalline product. The crystals were collected on a sintered-glass filter inserted into a side-arm of the reaction flask, and were washed with dry ether (3 × 20 ml.; introduced into the flask through a dropping funnel) before drying *in vacuo* over phosphorus pentoxide at room temperature.

Potassium methyl 1-methoxypicrate was prepared in 74% yield (Found: N, 12·2; K, 11·5 Calc. for $C_8H_8N_3O_8K,CH_3{\cdot}OH$: N, 12·2; K, 11·3%). The infrared spectrum of a sample mulled in Florube oil showed a strong band at 3567 cm.$^{-1}$, and a broad, weaker band at 3384 cm.$^{-1}$. Heating the sample at 78° *in vacuo* for 3 hr. did not remove the methanol of crystallization (Found: N, 12·0; K, 11·1%). The infrared spectrum still revealed hydroxyl bands. A sample was dissolved in acetone, reprecipitated by addition of benzene, washed with ether, and dried *in vacuo* at 20°. The infrared spectrum still showed methanol of crystallization (Found: N, 12·0%). Acetone of crystallization (Calc.: N, 11·8%) was absent since there was no carbonyl band in the infrared spectrum.

Potassium ethyl 1-ethoxypicrate, prepared in 85% yield, was dried *in vacuo* at 20° (Found: C, 35·5; H, 3·8; K, 11·5. Calc. for $C_{10}H_{12}N_3O_8K$: C, 35·2; H, 3·55; K, 11·5%). The infrared spectrum did not reveal alcohol of crystallization.

An attempted preparation of potassium methyl 1-phenoxypicrate, from phenyl picryl ether, yielded only potassium methyl 1-methoxypicrate (50%), identified by analysis (Found: K, 11·4%) and the infrared spectrum. Similarly, potassium ethoxide with phenyl picryl ether yielded potassium ethyl 1-ethoxypicrate (42%) which was also identified by analysis (Found: K, 11·4%) and the infrared spectrum.

Alcoholysis of Phenyl Picryl Ether.—Phenyl picryl ether (0·104 g.) was boiled for 90 min. with absolute methanol. The solvent was distilled off under reduced pressure to leave an oily crystalline residue (0·104 g.). Infrared analysis revealed 31 mole % of methyl picryl ether. A similar experiment with phenyl picryl ether and ethanol led to a 45% yield of ethyl picryl ether. The reaction in methanol was repeated in an alkali-etched flask, yielding 49% of methyl picryl ether. In each case, the infrared spectrum of the mixture showed that the remainder of the product was entirely phenyl picryl ether.

Analyses.—Samples of potassium methyl 1-methoxypicrate exploded violently during analysis for carbon and hydrogen. The explosion was slightly modified by mixing the sample with cupric oxide and omitting potassium dichromate, but reproducible analyses were not obtained. There was no explosion when potassium ethyl 1-ethoxypicrate was analysed for carbon and hydrogen in the presence of cupric oxide, but violent explosions occurred when potassium dichromate was added.

Infrared Spectra of Meisenheimer Complexes.—The infrared spectra of the complexes (0·5 mg. samples) were examined in potassium chloride discs. It was shown for potassium methyl 1-methoxy- and 1-ethoxy-picrate and for potassium ethyl 1-ethoxypicrate that the spectra of samples pressed in discs were identical with those of samples mulled in Nujol oil. The 3800—2700 cm.$^{-1}$ region was scanned with a Perkin–Elmer model 112 single-beam, double-pass

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[26] Massey and Philbrook, *J. Amer. Chem. Soc.*, 1951, **73**, 3454.

TABLE 1. *Infrared spectra of Meisenheimer complexes.*

Complex OR,OR′ in (II)	Frequencies (cm.$^{-1}$) and intensities of observed bands (vs = very strong, s = strong, m = medium, w = weak, vw = very weak)						
OEt,OEt	3090vw	1613s	1538m	1513s	1490s	1451m	
OEt,O·CH$_2$Ph ...	3090w	1603vs	1547m	1511vs	1481vs	1449m	
OEt,OPr^i	3089vw	1605s	1546m	1513vs	1484vs	1451m	
OEt,OMe	3090vw	1612s	1548m	1513s	1492s	1446m	
OMe,O·CH$_2$Ph ...	3085m	1608s	1550m	1517s	1487s	1450m	
OMe,OPr^i	3098vw	1600s	1534m	1511vs	1493s	1453m	
OMe,OMe	3090vw	1608s	1531m	1513s	1493s	1449w	
Cf. Pic·OMe	3092m	1616s 1610s	1541s	1511*w	1486m	1453w	
OEt,OEt	1408m	1377s	1332w	1297s	1253vs	1221vs	
OEt,O·CH$_2$Ph ...	1404vs	1374vs	1337w	1297s	1258vs	1220vs	
OEt,OPr^i	1406s	1376s	1332w	1299vs	1258vs	1208vs	
OEt,OMe	1409s	1374s	1345w	1299vs	1249vs	1222vs	
OMe,O·CH$_2$Ph ...	1408s	1373s	1332w	1295s	1239vs	1206vs	
OMe,OPr^i	1399m	1372m	1333w	1299s	1255vs	1209vs	
OMe,OMe	1404m	1379m	1333m	1297s	1238vs	1206vs	
Cf. Pic·OMe	1412m	1383*w	—	1299*w	1267m	1192m	
OEt,OEt	1152s	1122m	1091w	1053vs	1050*s	1011m	
OEt,O·CH$_2$Ph ...	1161m 1153m	1125w	1089w	1053vs	1049vs	1029m 1000m	
OEt,OPr^i	1163s	1122m	1085w	1057vs	1049vs	1031vs	
OEt,OMe	1157vs	1125m	1097m	1056s	1049s	1010m	
OMe,O·CH$_2$Ph ...	1178*s 1161s	1124m	1076s	1058vs	1045vs	1029s 1002*m	
OMe,OPr^i	1160*m	1122m	1083w	1062vs	1053s	1020s	
OMe,OMe	1161s	1124m	1096vw	1063s	1045s	1012w	
Cf. Pic.OMe	1163w	1124w	1087m	—	—	—	
OEt,OEt	933w	907m	813w	769w	750m	713w	694m
OEt,O·CH$_2$Ph ...	935m	907vs	815w	769w	746vs	714m	694m
OEt,OPr^i	934w	907s	818vw	771w	752m	713vw	696m
OEt,OMe	935m	908s	814w	762w	748s	714w	693m
OMe,O·CH$_2$Ph ...	932w	907s	818w	763w	742s	707s	690m
OMe,OPr^i	926vw	908m	815m	769w 763w	746m	713vw	694m
OMe,OMe	928w	908s	814w	763w	747m	714w	694m
Cf. Pic·OMe	937m	914m	826w	781m	743s	718s	679m

* Shoulder on neighbouring strong band.

Additional bands

OEt,OEt: 2972vw, 2907w, 2871vw, 1344vw, 942w, 871vw, 794vw, 731vw, 715*w
OEt,O·CH$_2$Ph: 2980w, 2873vw, 1393*s, 1136w, 945*w, 846m, 807*vw, 791vw, 778w, 757*m, 704s
OEt,OPr^i: 3053w, 2968m, 2874vw, 1111m, 971vw
OEt,OMe: 2984w, 2958m, 2908w, 2861w, 1529*m, 1464vw, 1435w, 941w, 805vw, 772vw, 757vw
OMe,O·CH$_2$Ph: 3025w, 2960*w, 2928m, 2873w, 1467*m, 1439*w, 992w, 969vw, 939*vw, 848w, 803*w, 775w, 751*m, 679*m
OMe,OPr^i: 3069vw, 2960w, 2778vw, 1553*w, 1437w, 1383*vw, 1342w, 953vw, 846vw
OMe,OMe: 3012vw, 2950w, 2849vw, 1437w, 970w, 943w, 792vw, 686m

TABLE 2. *Infrared analysis of synthetic mixtures of picryl ethers,* Pic·OR *and* Pic·OR′.

OR	Key band (cm.$^{-1}$)	Average deviation (%)	OR′	Key band (cm.$^{-1}$)	Average deviation (%
OMe	982	1·8	OEt	1006	1·7
OMe	982	1·3	OPh	1157 862	0·8
OMe	982	0·6	O·CH$_2$Ph	943	0·6
OMe	982	0·8	OPr^i	942	0·4
OEt	1006	0·5	OPh	1175 862	2·4
OEt	1006	0·6	O·CH$_2$Ph	—	—
OEt	1006	0·1	OPr^i	1379 942	1·0

spectrometer (calcium fluoride prism), and the 1800—670 cm.$^{-1}$ region with a Perkin-Elmer Infracord spectrometer (sodium chloride prism). The spectrum of potassium methyl 1-methoxypicrate was also examined in 0·096M-acetone solution in a 0·1 mm. cell, the model 112 spectrometer and calcium fluoride prism being used. Frequencies (cm.$^{-1}$) and apparent molar extinction coefficients were 1604 (680), 1552sh (270), 1542sh (320), 1520 (690), 1493 (605), 1313sh (260), and 1298 (405).

For results see Table 1.

Infrared Analysis of Picryl Ether Mixtures.—The infrared spectra of the picryl ethers, in chloroform solution, were recorded with the model 112 spectrometer, with a sodium chloride prism. The spectra of the picryl ethers, and of other picryl compounds, will be reported elsewhere. The key band, or bands, for each picryl ether were examined in a 0·1 mm. cell at 0·15, 0·08, and 0·05M-concentrations. Beer's absorption law was obeyed, the variation between the apparent extinction coefficients measured at these three concentrations not exceeding 6·0%. Duplicate determinations on the same solution showed similar variations. Two synthetic mixtures of each pair of picryl ethers (A and B) were analyzed, one mixture having a concentration ratio of 2A : B and the other A : 2B. Corrections were applied for overlap of the key band for one component by bands in the spectrum of the other. Overlap accounted for up to 25% of the total absorption at the key bands for isopropyl picryl ether in its mixtures with methyl and ethyl picryl ethers, but for less than 5% in the other ether mixtures. There was no suitable key band for estimation of benzyl picryl ether in the presence of ethyl picryl ether;

TABLE 3. *Meisenheimer addition compounds and the products of acid decomposition.*

					K (%)		Acid decomp. product	
Picryl ether	KOR	Solvent	Run no.	Yield (%)	found	calc.	Composition, mole (%)	Average composition
OMe	KOEt	EtOH	1	57	11·5	12·0	67·3 OEt 32·8 OMe	65·8 OEt 34·3 OMe
			2	51			64·2 OEt 35·8 OMe	
OEt	KOMe	MeOH	1	39	9·5	10·0 *	66·4 OEt 33·6 OMe	65·0 OEt 35·0 OMe
			2	14			63·5 OEt 36·5 OMe	
OMe	$KO\cdot CH_2Ph$	$Ph\cdot CH_2\cdot OH$	1	51	8·6	7·9 †	42·0 OMe 58·1 $O\cdot CH_2Ph$	43·7 OMe 56·4 $O\cdot CH_2Ph$
			2	36			45·4 OMe 54·7 $O\cdot CH_2Ph$	
$O\cdot CH_2Ph$	KOMe	MeOH	1	28	9·5	9·7 ‡	43·3 OMe 56·7 $O\cdot CH_2Ph$	43·4 OMe 56·6 $O\cdot CH_2Ph$
			2	29			43·5 OMe 56·5 $O\cdot CH_2Ph$	
$O\cdot CH_2Ph$ §	KOEt	EtOH	1	50			34·1 OEt 65·9 $O\cdot CH_2Ph$	35·0 OEt 65·1 $O\cdot CH_2Ph$
			2	47			34·8 OEt 65·3 $O\cdot CH_2Ph$	
			3	47	9·4	9·7	36·0 OEt 64·0 $O\cdot CH_2Ph$	
OPr^i §	KOMe	MeOH	1	71	11·6	11·5	29·5 OMe 70·5 OPr^i	28·9 OMe 71·1 OPr^i
			2	52			28·2 OMe 71·8 OPr^i	
OPr^i §	KOEt	EtOH	1	60	11·0	11·0	36·9 OEt 63·1 OPr^i	36·8 OEt 63·2 OPr^i
			2	55			36·8 OEt 63·3 OPr^i	

* Calc. for 2 moles of methanol of crystallization. The infrared spectrum showed medium-strength bands at 3570 and 3450 cm.$^{-1}$.

† Calc. for 1 mole of benzyl alcohol of crystallization. The infrared spectrum revealed a weak bonded hydroxyl band at 3560 cm.$^{-1}$.

‡ Calc. for 1 mole of methanol of crystallization. The infrared spectrum showed a weak bonded hydroxyl band near 3560 cm.$^{-1}$.

§ These addition complexes have not previously been reported.

the benzyl ether was therefore determined by difference. Key bands, and average deviations from the known composition of synthetic mixtures, are shown in Table 2. Where more than one key band per component is used, the deviation quoted is that for the average of the calculated values.

Acid Decomposition of Complexes.—The addition complex (60—100 mg.) was shaken with benzene (20 ml.) and 0·1N-aqueous sulphuric acid (20 ml.); the red colour was immediately destroyed. The acid layer was extracted with more benzene (20 ml.). The combined benzene extracts were washed with water (20 ml.) and dried (Na_2SO_4). The benzene was distilled off and the last traces of solvent were removed at 20 mm. Benzyl alcohol, when present, was removed at 150°/20 mm. (oil-bath). The picryl ether residue was dissolved in a pipetted volume of spectroscopic-grade chloroform such that the concentration of each picryl ether was in the range 0·05—0·10 mole $l.^{-1}$. The infrared spectrum was then compared with that of a synthetic picryl ether mixture to check the absence of other components. The mixture of unknown composition was then divided into two portions, each of which was subjected to quantitative infrared analysis. The compositions listed for each acid decomposition in Table 3 are the averages of the two sets of values obtained.

DISCUSSION

Preparation of the Addition Complexes.—The complexes were prepared in anhydrous alcohol to avoid the hydrolysis known to occur in water.[20,27] The solutions were dilute to avoid forming complexes with more than one mole of base.[21,27] The addition complexes were moderately soluble in these solvents, even after addition of benzene, so that the yields of isolated product were often low. Potassium methyl 1-benzyloxypicrate crystallized only when kept at 0° for at least 30 min., which may explain the failure of Earle and Jackson [21] to add sodium benzyl oxide to methyl picryl ether. We could not isolate a product from the reaction of potassium benzyl oxide with ethyl picryl ether in benzyl alcohol solution; the product was colloidal, and attempts to isolate a crystalline complex were not successful.

The phenoxy-group was lost from phenyl picryl ether on treatment with alcoholic alkali, and on treatment with boiling methanol or ethanol. Farmer [28] also observed the displacement of the phenoxy-group in alkaline alcoholic solutions, but reported no displacement by boiling methanol or ethanol. This discrepancy can probably be attributed to traces of alkali from the glass flask. Repetition of the experiment in a flask which had previously been etched with alkali and then washed, first with acid and then with distilled water, led to an increased proportion of replacement of the phenoxy-group in methanol solution. Brady and Horton [29] have reported slight replacement of methoxy by ethoxy when methyl picryl ether is crystallized from ethanol, and a similar replacement when ethyl picryl ether is crystallized from methanol.

Several of the Meisenheimer addition complexes were isolated with methanol or benzyl alcohol of crystallization. Although Farmer [20] was able to remove the methanol of crystallization from potassium methyl 1-methoxypicrate at 75°, we were unable to achieve this *in vacuo* at 78°. The methanol of crystallization in this complex is unusual in that *two* bonded hydroxyl bands appear in the infrared spectrum, at 3567 and 3384 $cm.^{-1}$, although potassium analyses on three separate preparations indicated only one molecule of methanol.

Infrared Spectra and Structure of the Meisenheimer Complexes.—The complexes are believed to have the fully covalent structure (II), but a charge-transfer complex structure is also possible. In the latter case, the infrared spectra should, by analogy with those of

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[27] Gazzolo and Jackson, *Amer. Chem. J.*, 1900, **23**, 376.

[28] Farmer, *J.*, 1959, 3430.

[29] Brady and Horton, *J.*, 1925, 2230.

known charge-transfer complexes,[30] closely resemble those of the parent picryl ethers, with, of course, the addition of the internal vibration frequencies of the added alkoxy-group. No additional bands would be expected in the region of the infrared examined here since no sufficiently strong bonds would be produced when the charge-transfer complex was formed.

The outstanding feature of the spectra of the complexes (Table 1) is the series of 5—6 bands of strong to very strong intensity between 1225 and 1040 cm.$^{-1}$, as well as a weaker band near 1090 cm.$^{-1}$. The picryl ethers show 5—8 bands in this region but, except for medium-intensity bands near 1192 and 1085 cm.$^{-1}$, these are quite weak. The covalent structure (II) is expected to show the characteristic strong bands of a ketal[31] at 1190—1158, 1143—1124, 1098—1063, and 1058—1038 cm.$^{-1}$. The complexes show bands at 1222—1206vs, 1163—1152ms, 1125—1122ms, 1097—1076m, 1063—1053vs, and 1053—1045s–vs, and four of these six strong bands do not appear in the spectra of the parent picryl ethers. The correspondence with the ketal bands clearly indicates that the complexes do have the fully covalent structure (II), and the appearance of these strong bands eliminates the possibility of a charge-transfer structure. Since the cyclopentadienyl anion includes a long conjugated system, it is likely that the bands at 1163—1152 and 1063—1053 cm.$^{-1}$ correspond to the out-of-phase and in-phase, in-plane, C–H deformations of the parent picryl compounds. Similarly, the out-of-plane C–H deformations appear near 910 and 750 cm.$^{-1}$. The ring stretching frequency near 1600 cm.$^{-1}$, which is double in the picryl ether spectra, is not resolved in the spectra of the complexes. The 3090 cm.$^{-1}$ C–H stretching band is extremely weak in the complexes, and thus could not be detected by Foster and Hammick[18] in the presence of Nujol oil The remaining regions of the spectra of the complexes are similar to those of the picryl ethers. Nearly all the other bands can be assigned to vibrations of the alkyl groups and, when present, to the alcohol of crystallization.

The transfer of negative charge to the ring which would accompany formation of either a charge-transfer complex or the Meisenheimer structure (II) will lead to a decreased N–O bond order of the nitro-groups, and thus to lowering of the asymmetric and symmetric N–O stretching frequencies.[32] As expected, the strong asymmetric N–O stretching band at 1552 cm.$^{-1}$ in the picryl compounds does not appear in the spectra of the complexes, which show a new band at either 1513 or 1489 cm.$^{-1}$. Although Foster and Hammick[18] assigned the lower band to the nitro-groups in potassium methyl 1-ethoxypicrate, it is not clear which of these two bands is a ring vibration. The medium-intensity band near 1536 cm.$^{-1}$ in the picryl ethers is still present in the complexes, and is believed to be due to ring C–C stretching. The 1347 cm.$^{-1}$ symmetric N–O stretching band of the picryl ethers is missing from the complexes. Potassium picrate has strong bands at 1332 and 1323 cm.$^{-1}$, but the complexes show only weak bands here. The transfer of negative charge to the nitro-groups is more complete in the complexes than in the picrate ion, and, in agreement with Foster and Hammick, the strong band near 1300 cm.$^{-1}$ can be assigned to the nitro-group.

Significance of the Meisenheimer Complexes.—The formation of the Meisenheimer complexes (Introduction, reaction 1) indicates that they are intermediates in activated nucleophilic substitutions. The kinetic objections to the covalent structure appear to be due to the fact that the structure of the transition state does not always approximate to that of the intermediate. However, the Meisenheimer complexes are characteristically intensely coloured, and it is significant that Chapman and Rees[13] observed no colour during the reaction of amines with halogenopyrimidines. It is possible that some activated aromatic nucleophilic substitutions do proceed through intermediates of the charge-transfer type. Although evidence for " built-in solvation " and base-catalysis has been

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[31] Bergmann and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

[32] Kross and Fassel, *J. Amer. Chem. Soc.*, 1956, **78**, 4225.

claimed [2,8] to support fully covalent intermediates, it does not discriminate against charge-transfer structures.

Acid Decomposition of Meisenheimer Complexes.—Addition of acids to the Meisenheimer complexes causes decomposition into both possible picryl ethers. If it is assumed that the action of the acid consists of irreversible removal of the anions produced by dissociation of the complex, then the proportions of the two picryl ethers will depend on the relative magnitudes of k_{-1} and k_{-2} (reaction 1). The production of an anion by dissociation of the complex is stated by Bunnett and Zahler [1] to depend upon the stability of the anion. Acid-decompositions have been reported of Meisenheimer complexes prepared by addition of alkoxide ions to picramides,[33] 1,3,5-trinitrobenzene,[21,27,34-36] and to picryl ethers (refs. 19, 20, 21, and present work), and by addition of amines to trinitrobenzene [37] and to picryl ethers.[33] In all cases, the nucleophile added to trinitrobenzene or picramide was quantitatively displaced by acids. The phenoxide ion is also much more readily lost than is methoxide or ethoxide (ref. 28 and present work), and methoxide ion is more readily lost than other alkoxide ions (refs. 19, 20, and Table 3). The ease of anion separation thus decreases in the order $PhO^- > OMe^- >$ other alkoxides $>$ amide ions $> H^-$. This order confirms the view that the relative stability of the anions produced is the chief factor determining dissociation of the complexes.

Table 3 reports the products formed in a number of acid-decompositions. The greater anionic stability of methoxide ion is confirmed. Although the carbon atom at the seat of substitution has sp^3-hybridization, so that the alkoxy-groups should not interact appreciably with the adjacent nitro-groups or with each other, steric effects do become apparent when bulky alkoxy-groups are present. Thus, while methoxide ion is lost from potassium methyl 1-ethoxypicrate twice as readily as ethoxide ion, the rates of loss of these two anions become more nearly equal when benzyl or isopropyl groups are present; presumably steric pressure assists the separation of the larger ethoxide ion. Loss of the bulky isopropoxy-group might be expected to be favoured, but there is no evidence for this. Possibly the two methyl groups adjacent to the oxygen atom decrease the anionic stability, in comparison to other alkoxide ions, by hindering solvation of the ion.

It is confirmed, by identity of the infrared spectra and of the mixtures of picryl ethers produced on treatment with acid, that potassium methyl 1-ethoxypicrate and potassium methyl 1-benzyloxypicrate can each be prepared from the two possible combinations of picryl ether and potassium alkoxide.

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UNIVERSITY OF MELBOURNE, PARKVILLE, N.2,
VICTORIA, AUSTRALIA.

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[34] Lobry de Bruyn, *Rec. Trav. chim.*, 1895, **14**, 84.

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[36] Ainscough and Caldin, *J.*, 1956, 2546.

[37] Hepp, *Annalen*, 1882, **215**, 356; Foster, *J.*, 1959, 3508; Hoffmann and Kirmreuther, *Ber.*, 1910, **43**, 1764.