vention adopted here for expressing the values of the acid dissociation constants. The *activity* of the hydrogen ion as obtained from measurements with a glass electrode was used together with the concentration ratio of the base to acid form of the ligand, so that,

$$K_a = a_H \quad (A)/(HA) \qquad (22)$$

The values will differ from those of the true concentration constants by the activity coefficient of the hydrogen ion appropriate to the medium employed, and will differ from the thermodynamic constants by the activity coefficient ratio of the base to acid forms.

It should be emphasized that as long as an appropriate correction is made for the free hydrogen ion concentration of the solution when this term is not negligible, no error in the complex formation constants results. The complex formation constants are true concentration constants.

Any arbitrary pH scale may be used without influencing the values of the complex formation constants as long as the data are internally consistent. To make the pK_a values more meaningful relative to others reported in the literature, we have standardized the Radiometer 25 SE pH meter used in these studies against NBS standard buffers.

The relatively high values of β_{22} obtained with Ni(II) and Zn(II) ions indicate that the bis imine complexes tend to form simultaneously with the mono imines. Such behavior is not likely to occur with Cu(II) (*2*, *3*) owing to its small tendency to attain a coordination number greater than four. The distribution of the Zn(II) species during the titrations represented by curves 2 and 5 of Figure 2 has been calculated and plotted in Figure 3. The extensive over-lap of higher and lower complexes is quite apparent. The most important complexes are the protonated imines and, in more alkaline solutions, $ZnP_2G_2^{-2}$. The binary glycinato complexes are formed only to a minor extent and those of pyridoxal are negligible. While certainly the distribution with valine is expected to be different it should be pointed out that the high amino acid levels used in the earlier work (*3*) will favor, in the more alkaline solutions employed, the disproportionation,

$$2MPV + HV \rightleftarrows M(PV)_2^{-2} + MV^+ + H^+$$

Thus, the constants reported in (*3*) probably are subject to some error.

The similar independently determined values of K_{aMPGH} for Ni(II) and Zn(II) found in this work and by Christensen (*1*) demonstrate a striking insensitivity to the strength of the metal–imine bond. Since this is the case, then certainly the considerably smaller interligand effects transmitted via the metal ion must be negligible as has been assumed. This insensitivity may result from a high ionic character in the metal ion–phenoxide ion bond. Our values for K_{aMPGH} lie between those reported by Christensen (*1*) and those reported by Davis, *et al.* (*3*). However, even Christensen's values may be considered only approximate since dissociation of the complexes to give lower species had not been taken into account.

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Preparation, Stability, and Use of Preformed Solutions of Iodine Isocyanate

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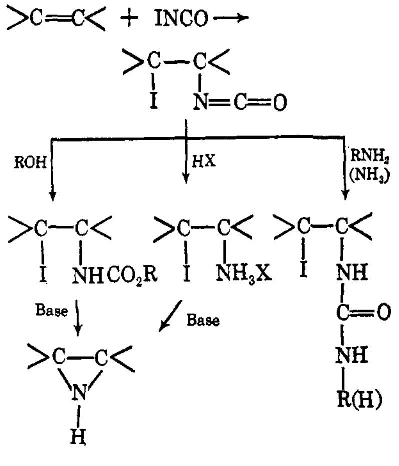
▶ Solutions 0.4 to 0.5N in iodine isocyanate (INCO) were prepared at −30° C. in the dark in ether, tetrahydrofuran (THF), and glyme by reaction of an excess of pure silver cyanate with iodine. Rate of generation of INCO is highest in glyme (30 minutes), next in THF (60 minutes), and slowest in ether (120 to 180 minutes). Decomposition of INCO at −11° C. is highest in glyme (75% decomposition in 24 hours) but considerably slower in THF and ether (15 to 25% decomposition in 24 hours). A differential iodometric analytical method has been developed for determining iodine and INCO in solution, thus permitting the generation, decomposition, and consumption of INCO in reactions to be accurately monitored. Preformed INCO solutions react extremely rapidly with many types of unsaturated compounds; the rate is at least ten times that observed in the conventional *in situ* reaction method. Care must be taken in storing and handling INCO solutions, as decomposing INCO solutions generate an unknown, colorless gas and slowly precipitate a mildly explosive white solid.

IODINE isocyanate (INCO), a reactive pseudohalogen readily prepared by the reaction of silver cyanate with iodine in dry ether, is a useful reagent for forming carbon-nitrogen bonds from a wide variety of unsaturated compounds (*1*, *2*, *4*–*6*). The addition reaction is a typical electrophilic reaction (*2*, *3*, *5*), proceeding by stereospecific *trans*-addition of INCO to the double bond (*6*). The initial reaction products are vicinal iodoisocyanates, readily converted to carbamates, amines, ureas, and aziridines:

$$AgCNO + I_2 \rightleftarrows INCO + AgI$$



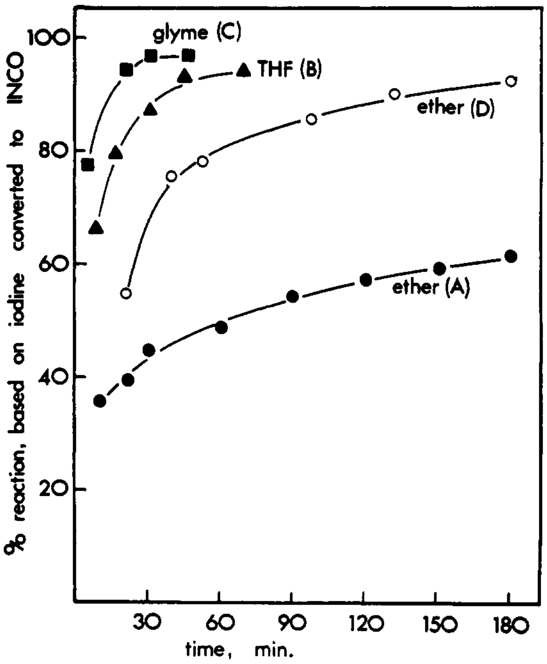


Figure 1. Generation of INCO

A. In ether
B. In THF
C. In glyme
D. In ether, ratio of reactants 3.4 to 1

For preparative purposes, INCO is customarily generated and allowed to react in a stirred heterogeneous system consisting of ether, silver cyanate (excess), iodine, unsaturated compound, and silver iodide, the other product of reaction of silver cyanate with iodine. Because the *in situ* procedure is the one most commonly used, in previous investigations (*4,5*) we studied the relative rates of addition of INCO in such a system to unsaturated compounds of widely varying structures. The relative rates we obtained in heterogeneous medium although internally consistent and readily duplicated, are of only qualitative value. We desired, therefore, to determine the kinetics of reaction of INCO with unsaturated compounds in homogeneous medium. Since ether is not the most desirable solvent for kinetic studies, we became interested in the question of the generation and stability of INCO in other solvents, and the use of such solvent systems not only in kinetic studies but in addition reactions as well. Finally, since no spectral data on INCO were available in the literature, we hoped to obtain such information also.

On the basis of early work of Birckenbach and Linhard (*1*), ethers appeared to be the most promising solvents to examine. The present paper describes the preparation, stability, use, chemical analysis, and infrared spectral characteristics of INCO in ether, tetrahydrofuran (THF), and ethylene glycol dimethyl ether (glyme).

DETERMINATION OF INCO IN PRESENCE OF IODINE

To follow the generation, stability, and consumption of INCO in reactions, an analytical procedure must be fast, accurate, complete, and reproducible. Birckenbach and Linhard (*1*) determined INCO in the presence of iodine by alkaline or acidic hydrolysis methods and also by gravimetric analysis in which silver cyanate, formed from INCO by reaction with silver nitrate, is weighed. All these procedures are time consuming and unsuitable.

METHOD ADOPTED. INCO is generated in the dark from iodine and excess silver cyanate at or below −15° C. in the solvent under study and small portions of the solution are filtered periodically by means of a filter stick into a chilled low actinic Erlenmeyer flask (or a flask wrapped in aluminum foil) maintained at or below reaction temperature. Total iodine plus INCO is determined by iodometric analysis of an aliquot part of the solution (usually 1 ml.). INCO alone is determined by adding an identical aliquot of the solution to a large molar excess of a reactive olefin (ca. 2 ml.) known to react rapidly and quantitatively with INCO but not with iodine (*5*), followed by iodometric determination of residual iodine. The difference between the titrations permits calculation of the normality (or molarity) of INCO. Suitable olefins are 2-methyl-1-pentene and tetramethylethylene.

In the initial experiments, however, vinyl acetate was selected as the unsaturated compound for determination of INCO, as it meets the requirements of high speed and quantitative addition [GLC analysis (*5*)], and iodine does not disappear in its presence. Considerable time was wasted using vinyl acetate, as, unfortunately, the INCO addition product, separately prepared, is labile and readily reliberates iodine on reaction with potassium iodide acetic acid.

Generation of INCO in Ether, THF, and Glyme. In control experiments it was first determined that solutions of iodine in the three highly purified, dry solvents are stable in the dark at −15° C. and below. The normality of the solutions, determined iodometrically, agreed with that calculated and remained constant over the time span of the experiments described below. It was similarly determined that iodine does not add to the olefins studied in this work.

When commercial silver cyanate of the best quality was added, however, and the development of INCO was followed as a function of time, the total titer of the solution (I_2+INCO) quickly dropped about 20% below the calculated value, whereas it should have remained constant in the absence of side reactions that consume positive halogen. Also, results were irreproducible. With fresh silver cyanate prepared by us, however, little (<5%) or no loss of positive halogen was observed over the time span of the experiments. In all of the results described in this paper, therefore, the silver cyanate used was freshly prepared from silver nitrate and potassium cyanate (*6*). Pure silver cyanate is a white solid, stable for long periods in the dark. Commercial samples, on the other hand, are invariably light gray to tan and must obviously contain impurities that cause destruction of positive halogen.

Figure 1 shows the rate of generation of INCO in ether (curves *A* and *D*), THF (curve *B*), and glyme (curve *C*) at −30° to −34° C. in the dark. The molar ratio of silver cyanate to iodine was 1.7 to 1 in *A*, *B*, and *C*, and 3.4 to 1 in *D*. The molar ratio of 1.7 to 1 was selected and used in most of our work, as that corresponds to the ratio employed in preparative work (*1*, *2*, *4–6*). The main conclusions are:

Generation of INCO is slowest in ether, the solvent universally employed in preparative work by previous workers.

In ether, at a molar ratio of AgOCN:I_2 of 1.7 to 1, the equilibrium concentration of INCO corresponds to only about 60% of that calculated (curve *A*). To achieve substantially complete (>90%) conversion of I_2 to INCO, a molar ratio of 3.4 to 1 is required (curve *D*).

In glyme, the fastest solvent of those studied, generation of INCO is substantially quantitative (>95%) in about 30 minutes (curve *C*).

In THF 94% of the calculated quantity of INCO is produced in about 60 minutes (curve *B*).

For preparative work therefore, on addition of INCO to double bonds either glyme or THF would appear to be the solvents of choice rather than ether. (Use of these solvents in double bond

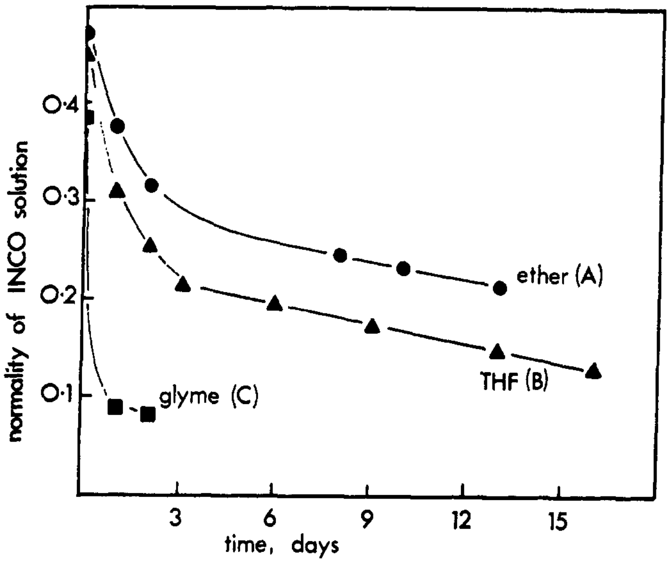


Figure 2. Decomposition of solutions of INCO at −11° C.

A. In ether
B. In THF
C. In glyme

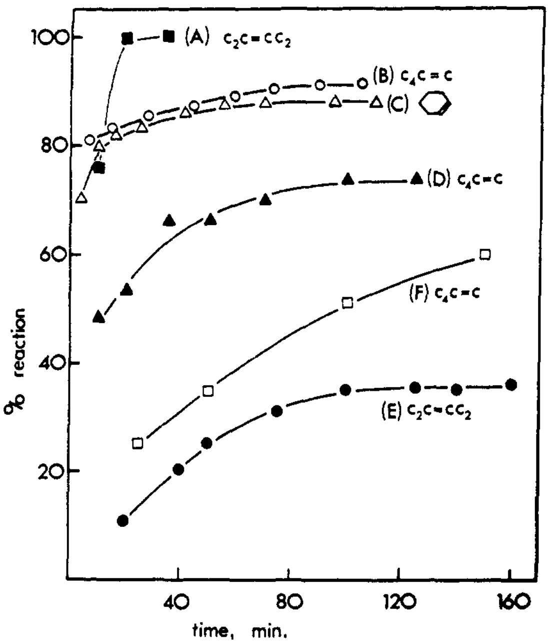


Figure 3. Rate of reaction of preformed solutions of INCO

A. In ether with *trans*-3-hexene at −45° to −47° C.
B. With 1-hexene at −45° to −47° C.
C. With cyclohexene at −45° to −47° C.
D. With 1-hexene at −69° C.
E. With *trans*-3-hexene at −47° C. by *in situ* method
F. With 1-hexene at 4° C., by *in situ* method

additions in heterogeneous and homogeneous media is discussed below.)

Decomposition of INCO in Ether, THF, and Glyme. Figure 2 shows the rate of decomposition of INCO in these solvents at −11° C. in the dark. The main conclusions are:

INCO is most stable in ether (curve *A*), only slightly less stable in THF (curve *B*), but unstable in glyme (curve *C*). Although not shown on the figure, no disappearance of INCO at −30° and −47° C. was observed in either solution over 5 hours and it is assumed that similar results would be obtained in THF. Glyme was not studied at these low temperatures.

The order of the solvents in rate of decomposition of INCO is the opposite of that for its generation.

At −11°, INCO solutions in ether or THF should not be stored for more than about 2 days.

A plot of the reciprocal of the concentration of INCO against time over a two- to three-week period gives a straight line after the first 1 to 2 days, suggesting a second-order decomposition in ether and THF. At this time no further conclusions can be drawn concerning the decomposition kinetics.

Care must be taken in handling and storing solutions of INCO. A colorless gas is slowly evolved and a mildly explosive white solid is precipitated.

In the first stability study we conducted, a tightly sealed brown bottle was used; after about 3 days' storage in the dark at −11° the bottle ruptured. In subsequent experiments, the storage flasks were equipped with a fermentation tube containing mineral oil which permitted gas to escape but prevented entry of moisture. Also, the flasks were wrapped in cotton and maintained in snugly fitting polyethylene containers. During storage, INCO solutions become brown as iodine is re-formed and a solid precipitates. This solid may explode if touched with a hypodermic needle or pipet, evolving a puff of purple vapor (iodine?). The composition of neither the gas nor the solid is yet known. Also low temperature evaporation of solutions of INCO produces a bown solid which decrepitates.

During the decomposition of INCO, the iodine titer increases at the expense of INCO, although total iodine plus INCO stays sensibly constant when pure dry reagents are employed. Birckenbach and Linhard (*1*) have suggested the following reaction sequence for decomposition of INCO in ether solution:

$$\mathrm{INCO} + C_2H_5OC_2H_5 \rightarrow \mathrm{HI} + \mathrm{OCNC_2H_4OC_2H_5}$$

$$\mathrm{HI} + \mathrm{INCO} \rightarrow I_2 + \mathrm{HOCN}$$

Trimerization of cyanic acid would be expected to yield cyanuric acid, an insoluble nonexplosive white solid.

Although we have no evidence for the following conclusion, the explosive white solid may be the unknown cyanogen peroxide produced by disproportionation of INCO:

$$2\,\mathrm{INCO} \rightarrow I_2 + \mathrm{N{\equiv}C{-}O{-}O{-}C{\equiv}N}$$

This reaction could account for decrease in INCO, increase in iodine, and the formation of a presumably explosive substance. Also, it would suggest second-order kinetics for decomposition.

INFRARED SPECTRAL STUDIES

Infrared absorption spectra were obtained on solutions of INCO during its generation and decomposition. It was necessary to obtain the spectra at the temperature of the instrument (30° to 35°), even though it was recognized that INCO was unstable at that temperature. It was assumed that within the short period required to obtain a spectrum in the 1900- to 2400-cm.$^{-1}$ region, the only region of any absorbance, little or no decomposition would occur. This conclusion appeared to be correct for ether and THF solutions. The major problem that developed was the nonuniform evaporation of ether when the cells were not tightly sealed. However, the spectra in the three solvents could be readily duplicated, they were internally consistent, and we believe they are reliable.

The infrared spectrum of freshly prepared INCO in ether shows only two absorption peaks, one at 2180 cm.$^{-1}$ (medium-strong) and one at 2250 cm.$^{-1}$ (weak). In THF, the bands at 2180 and 2250 cm.$^{-1}$ are present, as well as one at 2330 cm.$^{-1}$ In glyme, the spectrum is much more complex, probably because of rapid decomposition in the

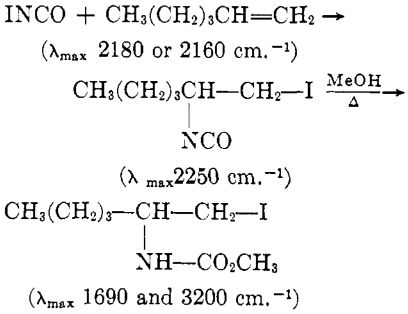
Table I. Reaction Conditions

Fig. 3, curve	Olefin	Reaction temp., ° C.	Molar ratio, INCO/olefin	INCO normality
A	*trans*-3-Hexene	−45 to −47	1.53/1.00	0.41
B	1-Hexene	−45 to −47	1.00/2.12	0.45
C	Cyclohexene	−45 to −47	1.00/1.01	0.38
D	1-Hexene	−59	1.83/1.00	0.36
E	*trans*-3-Hexene	−47	1.30/1.00/0.67[a]	*in situ*
F	1-Hexene	+4	1.33/1.00/0.88[a]	*in situ*

[a] Molar ratio of reactants AgOCN/I_2/olefin. Olefin molarity in ether 0.14 (3-hexene) and 0.23 (1-hexene).

spectrophotometer, but maxima are present at 2160 and 2250 cm.$^{-1}$, as well as at 1965, 2000, and 2350 cm.$^{-1}$

The absorption maximum at 2180 cm.$^{-1}$ in ether and THF and at 2160 cm.$^{-1}$ in glyme is attributed to INCO on two grounds. First, during a decomposition study in ether and in THF over a 2-week period and in glyme for several days at −11°, a rough correlation was obtained between the absorbance at that wavelength and the concentration of INCO determined chemically. Second, when an excess (3 ml.) of *trans*-3-hexene or 2-methyl-1-pentene is added to 1 ml. of an approximately 0.5*N* INCO solution, the absorption band at 2180 cm.$^{-1}$ completely disappears within 1 minute and that at 2250 cm.$^{-1}$ undergoes a substantial increase in intensity. This result is readily explained by addition of INCO to the double bond to produce a vicinal iodoisocyanate which is known to absorb at 2250 cm.$^{-1}$, as has been shown in numerous other cases (*5*). Further, addition of methanol (3 ml.) to the solution of the iodoisocyanate followed by heating for 30 minutes on the steam bath completely eliminates the 2250-cm.$^{-1}$ band and produces the expected carbonyl (1690 cm.$^{-1}$) and N-H (3200 cm.$^{-1}$) bands of a vicinal iodocarbamate (illustrated with 1-hexene):



$$\mathrm{INCO} + \mathrm{CH_3(CH_2)_3CH{=}CH_2} \rightarrow$$

$$(\lambda_{\max}\ 2180 \text{ or } 2160 \text{ cm.}^{-1})$$

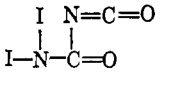
$$\mathrm{CH_3(CH_2)_3}\underset{\displaystyle \mathrm{NCO}}{\underset{|}{\mathrm{CH}}}\mathrm{-CH_2-I} \xrightarrow[\Delta]{\mathrm{MeOH}}$$

$$(\lambda_{\max} 2250 \text{ cm.}^{-1})$$

$$\mathrm{CH_3(CH_2)_3}-\underset{\displaystyle \mathrm{NH-CO_2CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2-I}$$

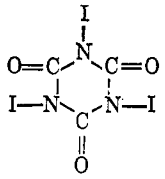
$$(\lambda_{\max}\ 1690 \text{ and } 3200 \text{ cm.}^{-1})$$

The absorption band at 2250 cm.$^{-1}$ always found in infrared spectra of INCO solutions is assumed to be caused by substances containing the $-\overset{|}{\underset{|}{\mathrm{C}}}-$ NCO system. There are several possible structures that could account for that band, one of which has been discussed—namely, the reaction product of INCO with the "ether" solvent. Other alternatives are the dimer of INCO (I), also suggested as a reaction product by Birckenbach and Linhard (*1*), and the trimerization product (II). No evidence is available to support any of the structures.



Dimer

(I)



Trimer

(II)

RATE OF REACTION OF PREFORMED SOLUTIONS OF INCO WITH UNSATURATED COMPOUNDS

Figure 3 shows the extent and rate of reaction of preformed filtered solution of INCO in ether with three olefins (curves *A*, *B*, *C*, and *D*) and also compares the rate of reaction of *trans*-3-hexene and 1-hexene with INCO by the conventional *in situ* method (curves *E* and *F*). Table I gives the pertinent reaction conditions for the results in Figure 3.

The most striking result shown in Figure 3 is the extremely high rate of reaction of unsaturated compounds with preformed solutions of INCO compared to that by the *in situ* method. (Other rate studies not shown in the figure are also consistent with that conclusion.) Rates of reaction with preformed INCO were so high in the temperature range that we could handle conveniently that a detailed kinetic study has been postponed until techniques are improved for handling and analyzing more dilute solutions of INCO and unsaturated compounds at low temperatures. With 1-hexene at −69° (curve *D*), however, the rate is not excessively high. A plot of reciprocal of the concentration of INCO against time gives a moderately good straight line, suggesting that the addition reaction is second-order. In another study, we hope to investigate the kinetics thoroughly and obtain the activation parameters.

Only qualitative rate comparisons can be made at this time but with preformed INCO solutions, reaction rates are conservatively estimated to be at least ten times greater than by the *in situ* method. Similarly, high reaction rates are obtained with THF and glyme. Rates are also high when the unsaturated compound is added to the unfiltered heterogeneous system containing the equilibrium concentration of INCO. Excess silver cyanate and iodine appear to have little or no effect on rate.

Ethyl crotonate, on the other hand, a compound that does not react with INCO by the *in situ* method (*4*, *5*), reacted to the extent of only 10% even with a preformed solution of INCO in the temperature range −45° to +25°.

Use of Preformed INCO for Preparative Purposes. It was confirmed that there is in fact a 1 to 1 molar correspondence (±5%) between INCO and olefin consumption. Experiments were conducted with both an excess and a deficiency of INCO (see Table I). When at least 1 mole of INCO was provided per mole of double bond, 90 to 100% reaction was obtained with cyclohexene *trans*-3-hexene and 1-hexene at or above −45° within 20 to 100 minutes (Figure 3). (Results with other unsaturated compounds were similar but are not shown in the figure.)

For preparative work there are some advantages in adding the unsaturated compound to the heterogeneous equilibrium solution of INCO rather than to the filtered solution, although the final results are the same (product quality and yield): Low temperature filtration is avoided with its attendant problems and high volume loss when a filter stick is used and completion of the reaction is readily observed visually by the change of color of the solution from brown to canary yellow or even colorless when a slight excess of reactive unsaturated compound is used. Since silver cyanate and iodine are both present, removal of INCO from solution by reaction causes more to form and ultimately consumes all the iodine (excess silver cyanate is always present). On the other hand, when a filtered solution of INCO is used (silver cyanate absent) the solution remains brown throughout because of residual iodine.

The preferred preparative procedure, therefore, is to generate the equilibrium concentration of INCO from silver cyanate and iodine (1.7 to 1 molar ratio) in THF or glyme at −30° (30 to 60 minutes) followed by addition of unsaturated compound preferably in slight molar excess over INCO. Reaction is complete even at −30° within 10 to 60 minutes in many cases and, for all practical purposes, instantaneously at higher temperatures (−10° to 0°) Completion of reaction is ascertained by color change, GLC (olefin disappearance), chemical analysis (INCO), and/or infrared spectrometry. [In following the extent of reaction GLC almost always indicates slightly higher results (5 to 10%) than INCO consumption owing presumably to postreaction in the chilled hypodermic syringe or the injection port.] The reaction solution is then filtered and the filtrate, often after evaporation of some or all of the solvent, is treated with methanol, hydrochloric acid, or ammonia, depending on the iodoisocyanate, to obtain the carbamate, amine hydrochloride, or urea, respectively. Yields of 80 to over 90% are the rule (see Experimental).

This procedure is recommended primarily for olefins that react relatively slowly, such as 1-hexene. By the *in situ* method, it is difficult to obtain complete reaction with such compounds because at the relatively high temperature required considerable decomposition of INCO occurs. With preformed INCO, on the other hand, a high rate of reaction is obtained even at low temperatures (Figure 3). The use of preformed INCO solutions is also preferred in cases where iodine may add across the double bond in competition with INCO. Preformed solutions of INCO contain only small quantities of unreacted iodine. Finally, as will be described in a subsequent publication, INCO adds readily to acetylenic compounds and dienes but the addition reaction is not satisfactory by the *in situ* method because of the facile addition of iodine.

EXPERIMENTAL

Materials Used. Pure, resublimed iodine was used throughout. The silver cyanate was freshly prepared from silver nitrate and potassium cyanate (*6*). Yields were in excess of 90%. Anhydrous reagent grade ether was treated with sodium overnight; the solvent was decanted from the excess sodium and used directly. Tetrahydrofuran was treated with calcium hydride and the solvent was decanted and fractionally distilled from fresh calcium hydride. The main fraction was then stored in a brown bottle over calcium hydride and used as needed. Glyme was first dried over potassium hydroxide and the solvent was decanted and fractionally distilled from metallic sodium. The main fraction was then stored in a brown bottle over calcium hydride.

The unsaturated compounds used—cyclohexene, *trans*-3-hexene, 1-hexene, 2-methyl-1-pentene, norbornene, vinyl acetate, tetramethylethylene, and ethyl crotonate—were the purest laboratory grades. All showed a single peak on GLC analysis, usually with a 20-foot, 15% Apiezon L stationary phase on ABS 70/80 mesh.

Determination of INCO in Presence of Iodine. Total I_2 + INCO. To an iodine flask containing 2 ml. of saturated aqueous potassium iodide 1 ml. of the solution to be analyzed was added, followed by 15 ml. of glacial acetic acid. After 20 seconds, 50 ml. of water was added and the iodine was titrated with 0.1 or 0.05*N* sodium thiosulfate solution. This volume of sodium thiosulfate is A.

Unreacted Iodine. To an iodine flask containing 2 ml. of 2-methyl-1-pentene (or tetramethylethylene), 1 ml. of solution was added. After 1 minute, 15 ml. of glacial acetic acid and 2 ml. of saturated aqueous potassium iodide were added. After 20 seconds, 50 ml. of water was added and the iodine was titrated as above. This volume of sodium thiosulfate is B.

Normality of INCO = (A − B) (normality of $Na_2S_2O_3$ solution). The maximum normality of INCO solutions prepared was about 0.5 *N*.

Generation of INCO Solutions. Typical Procedure. Five grams of iodine (0.02 mole) was dissolved in 100 ml. of dry, peroxide-free solvent in a three-necked flask wrapped in aluminum foil and equipped with a stirrer and thermometer. The solution was cooled to −30°, several 1-ml. aliquots were withdrawn, and the iodine content was determined in replicate. The average value obtained agreed with that calculated from the weight of iodine added to ±2%. In other controls, it was shown that the iodine concentration did not diminish in the presence of the olefins whose rates of reaction were studied (silver cyanate absent).

Five grams of silver cyanate (0.034 mole) was added in one portion to the stirred solution. Aliquots were removed at frequent intervals using a chilled pipet and the titration procedure described above was used. With ether as solvent, the use of 10 grams of silver cyanate (0.067 mole) was also studied; this quantity was required to obtain over 90% conversion of I_2 to INCO. Figure 1 summarizes the results. Although not shown in the figure, the sum of I_2 + INCO remained sensibly constant throughout the time span of the generation experiments (maximum diminution, 5%).

Decomposition of INCO Solutions. Typical Procedure. The INCO solutions were filtered at −30° by means of an aspirator and filter stick into chilled low actinic Erlenmeyer flasks wrapped in aluminum foil. A maximum of 3 minutes was required for filtration. The I_2 and INCO concentrations of the filtered solutions immediately after filtration were identical with the values just before filtration. The Erlenmeyer flasks, equipped with a gas escape valve, were then wrapped in cotton and placed in snugly fitting polyethylene containers for storage at −11°. For convenience in sampling, the top of the Erlenmeyer flask was outside the storage container; the main body of the solution, however, remained in the dark and was protected at all times. Samples were withdrawn at intervals and the I_2 and INCO contents determined as above. Results are summarized in Figure 2.

Infrared Spectral Studies. A Perkin Elmer 137-B Infracord spectrophotometer was employed, using 0.05-mm. matched cells.

Rate of Reaction of Preformed INCO Solutions with Unsaturated Compounds. Reactions were followed by chemical analysis (disappearance of INCO), gas-liquid chromatography (disappearance of unsaturated compound), and infrared spectrometry (disappearance of 2180 or 2160-cm.$^{-1}$ absorption band). The three methods were not employed every time; the first method was always used. The unsaturated compound (cyclohexene, *trans*-3-hexene, 1-hexene, or ethyl crotonate) was added in one portion to the solution of INCO maintained at the temperature indicated in Figure 3. In all cases, INCO solutions containing about 95% of the calculated quantity based on I_2 were separated by filtration from excess silver cyanate and silver iodide to obtain homogeneous solutions. In several instances, for comparison purposes, the olefin was added to the heterogeneous system as soon as the equilibrium concentration of INCO had been formed.

To ascertain that a 1 to 1 molar correspondence exists between INCO and olefin disappearance, as the literature suggests, experiments were conducted with both an excess and deficiency of INCO. A typical experiment is detailed below, in which a 50% molar excess of INCO was used with *trans*-3-hexene added in one portion at −47° and reaction allowed to proceed until the INCO concentration stabilized.

Before Reaction (100 ml. of ether solution)	
Normality of I_2 + INCO	0.446 ± 0.003
Normality of I_2	0.038 ± 0.001
Normality of INCO	0.408
Molarity of INCO	0.204
Equivalents of INCO available	0.0408
Moles of INCO available	0.0204 (A)
Equivalents of *trans*-3-hexene added	0.0266
Moles of *trans*-3-hexene added	0.0133 (C)
After Reaction	
Normality of I_2 + INCO	0.165
Normality of I_2	0.038
Normality of INCO	0.127
Equivalents of INCO unconsumed	0.0127
Moles of INCO unconsumed	0.00635 (B)
Equivalents of INCO consumed	0.0281
Moles of INCO consumed	0.0141 (A − B)

The percent reaction can then be calculated in various ways: One way is:

$$\% \text{ reaction} = \frac{A - B}{C} \times 100 = \frac{0.0141}{0.0133} \times 100 = 105\%$$

In replicates of the above, the extents of reaction calculated ranged from 95 to 105%. Reaction was usually complete within 15 minutes. GLC results showed a slightly higher extent of reaction before completion, but leveled off at 100% (complete disappearance of olefin with excess INCO) with the more reactive olefins.

Use of Preformed INCO Solutions for Preparative Purposes. TYPICAL PROCEDURE FOR GLYME. A solution 0.431*N* in INCO and 0.03*N* in iodine was obtained in 35 minutes at −35° from 5 grams (0.02 mole) of iodine, 5 grams (0.034 mole) of silver cyanate and 100 ml. of glyme. To the stirred unfiltered system, 1.94 grams (0.023 mole) of *trans*-3-hexene was added in one portion. Within 30 minutes at −35°, the solution became colorless; chemical analysis showed that 97% of the calculated quantity of INCO, based on the original quantity of iodine employed, had been consumed. The solution was filtered, the precipitated salts were washed with a small quantity of glyme, and 30 ml. of 17% aqueous hydrochloric acid was added to the combined filtrate and washings. Carbon dioxide was evolved and a slight exotherm was noted. After 2 days at room temperature the solution was evaporated to dryness and the solid residue was washed with a small quantity of ether and filtered. The insoluble residue, consisting of 3-iodo-4-aminohexane hydrochloride, was a pale yellow solid that weighed 4.08 grams (83% based on iodine) (m.p. 150–1°). Recrystallization from ethanol merely sharpened the melting point to 151° [literature (*5*) 151°] and removed a little color. Infrared spectra of the crude and pure iodoamine hydrochloride were identical with that of a known analytically pure specimen.

FOR THF. A solution 0.376*N* in INCO and 0.091*N* in iodine was prepared as described above from 4 grams each of iodine and silver cyanate in 80 ml. of THF. Equilibrium was reached in 70 minutes. The solution was filtered at −47°, but only 51 ml. of INCO solution could be removed by the filter stick technique. To this solution, 0.891 gram (0.0108 mole) of cyclohexene was added and after 40 minutes at −47° the calculated quantity of INCO had disappeared. To ensure complete reaction, an additional 2 grams of cyclohexene was added and the solution was allowed to stand overnight in a Dewar flask (temperature was +10° the next morning). The brown solution was evaporated to dryness in a rotary evaporator and the residue was refluxed for several hours with 150 ml. of methanol. Re-evaporation to dryness yielded a brown solid residue that was dissolved in ether. The ether solution was washed with 2% aqueous sodium bisulfite solution to destroy iodine and then several times with water. Evaporation of the ether yielded 2.35 grams (92% yield) of methyl (*trans*-2-iodocyclohexyl)carbamate (m.p. 122–26°). Recrystallization from methanol gave the analytically pure product [m.p. 134°, literature (*1*) 135°]. Infrared and NMR spectra were identical with those of a known specimen and agreed exactly with literature reports (*6*). Similar results were obtained with an ether solution of INCO.

FOR ETHER. To the reaction solution of excess *trans*-3-hexene and INCO described above, a larger molar excess of concentrated hydrochloric acid was added and the solution was allowed to stand overnight at room temperature. The ether and excess acid were evaporated and the residue was treated with a minimum quantity of 10% aqueous sodium bisulfite solution to destroy the iodine. Cold methanol was then added to precipitate the 3-iodo-4-aminohexane hydrochloride (m.p. 150–1°) (59% yield). Its infrared spectrum was identical with that of an authentic, analytically pure specimen.

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